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(54) Title: PROCESS AND CATALYSTS FOR THE METHANATION OF OXIDES OF CARBON

## (57) Abstract

The present invention is directed to catalysts for the conversion of oxides of carbon to methane and/or other hydrocarbons and to precursors of such catalysts. The catalyst precursors include one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth containing perovskites, the precursor including nickel or nickel cations sufficient for a catalyst obtainable by reducing the precursor to be capable of at least partially reducing an oxide of carbon to a hydrocarbon product. Processes for the preparation of such catalysts and catalyst precursors are also disclosed, as are processes for the conversion of oxides of carbon to methane and/or other hydrocarbons.

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## Process and catalysts for the methanation of oxides of carbon

### Field of the Invention

This invention relates to processes and catalysts for the conversion of oxides of carbon to methane and/or other hydrocarbons, and to processes for making such catalysts, and to precursors of such catalysts.

### Background of the Invention

Human activities are substantially increasing the atmospheric concentrations of greenhouse gases, such as carbon dioxide, compared with pre-industrial times. The increasing trend in emissions is expected to continue and accentuate the natural greenhouse effect, with wide ranging potential impacts on the natural environment and socio-economic systems. This human induced warming is known as the 'enhanced greenhouse effect'.

Carbon dioxide is the major greenhouse gas arising from anthropogenic sources. It is released mainly by burning fossil fuels (oil, coal, natural gas) in electric power generation, blast furnaces and automotive vehicles. Only about half of these carbon dioxide emissions are absorbed by oceans, forests or otherwise. The remainder stays in the atmosphere, acting as a greenhouse gas. It is estimated that if the current rate of CO<sub>2</sub> emissions continues, the average global temperature will rise by 1.5 to 4.5°C over the next 40 to 50 years, without taking into account the warming caused by increases in other greenhouse gas concentrations.

Much political debate and controversy surrounds this issue but nonetheless, there exists widespread agreement that carbon dioxide emissions must be reduced. The use of renewable energy does not produce greenhouse gases and either does not pollute or emits far less pollution than burning fossil fuels. Renewable energy sources also represent a secure and stable source of energy for mankind. Renewable energy sources are those which do not run out or are replaced as quickly as they are used. Energy from the sun, wind, tides, geothermal and hydro electric sources are examples of renewable resources. Energy from waste, landfill gases, bagasse, plantation timber or other biological sources, if managed properly, can also be considered renewable. In contrast, fossil fuels form so slowly in comparison to our energy use that we are essentially mining finite, nonrenewable resources and could exhaust quality supplies within the foreseeable future.

The diversity and ready availability of biomass make it a strong alternative to fossil fuels for future energy requirements around the world. Currently, there are over 7000 megawatts of biomass power capacity installed at more than 350 plants in the U.S.,

from a diverse range of producers including the pulp and paper industry, electric utilities, and independent power producers. Sources of biomass used in power plants include wood residues (e.g. saw dust, sander dust, bark); agricultural waste (e.g. sugar cane bagasse, rice hulls); food processing residues (e.g. nut shells); and sludges (e.g. sewage, chemical, pulp & paper, bio-sludge). Significantly, biomass fuels are "environmentally friendly". In particular, they produce virtually no sulfur emissions, thus helping to mitigate acid rain; they "recycle" atmospheric carbon, hence minimising global warming impact; and they generate low NO<sub>x</sub> levels and create few particulates.

Gasification of biomass is an important technology in the primary conversion of biomass for electricity production. This latter process typically involves the partial oxidation of biomass to give a mixture of gases and organic vapours. After the gasification products are cleaned, the gas mix (termed "synfuel") can be introduced to a boiler or the combustion section of a turbine system. Synfuel is usually composed of a mixture of carbon monoxide, carbon dioxide, methane and hydrogen in addition to small concentrations of tars, alkali metals and sulfur compounds. For use of the synfuel in a gas turbine-based generation facility it is desirable to reduce explosion risk by minimising the concentration of hydrogen present in the synfuel. Consequently, an attractive route would be to react the oxides of carbon with the hydrogen present in the synfuel to produce methane. This approach can be represented by the following general reaction equations:



The formation of methane is in itself advantageous as it is an excellent fuel for power generation. Reactions of the type represented in equations (1) to (3) are collectively known as "methanation" reactions.

Another renewable energy source of particular interest is solar energy. Application of solar energy hinges on development of means to convert this diffuse and intermittent source of energy to forms amenable for transport and storage. Thermochemical energy conversion offers the potential to store and to transport solar energy at ambient temperature with the release of energy in the form of heat at temperatures up to 1000K and with overall efficiencies of about 90%. Chemical energy can be accumulated by utilizing heat of reaction in a reversible reaction. If a reaction proceeds endothermically then the same heat of reaction can be recovered from the

reverse reaction. The reaction of most interest in this respect is the carbon dioxide reforming reaction:



Thermochemical heat pipe systems using this reaction are shown in diagrammatic form in Figures 1 & 2. Figure 1 represents a closed loop configuration, and Figure 2 shows an open loop cycle. Briefly, in the closed loop configuration, concentrated solar energy is used to supply the process heat for the  $\text{CO}_2$  reforming reaction. Subsequently, the  $\text{CO}$  and  $\text{H}_2$  reaction products can be stored and/or transported to a separate site where the reverse methanation reaction is performed to release the stored solar energy. The methanation products are then recycled to the reformer reactor to complete the closed loop.

Alternatively, an open loop cycle can be employed, as illustrated in Figure 2. In this configuration the product syngas is combusted to produce heat and power (typically in a gas turbine system integrated to an IGCC power plant).

In summary, it can be seen that catalytic methanation is a central technology for power generation options involving the use of renewable energy sources such as biomass or solar energy. Consequently, there is a need to develop catalysts for the methanation process which exhibit excellent activity, stability, resistance to coking and economic viability. Desirably, such catalysts will be capable of catalysing the methanation reactions at atmospheric pressure or higher and relatively low temperatures while exhibiting sufficiently high activity, stability and resistance to coking to be useful in large scale operations.

Catalytic methanation is carried out in ammonia synthesis plants as a means of reducing the concentration of carbon oxides before the reactant gas enters the ammonia synthesis catalyst bed. Another application for methanation catalysts is in the production of substitute natural gas (SNG) from sources such as oil and coal. The main difference in these applications is the composition of the gas streams involved. For example, a typical gaseous feedstock entering the methanation reactor in an ammonia plant has the approximate composition 0.4%  $\text{CO}$ , 0.1%  $\text{CO}_2$ , 73.7%  $\text{H}_2$ , 24.4%  $\text{N}_2$ , 0.4%  $\text{CH}_4$  and 1%  $\text{H}_2\text{O}$ . In contrast, the gas stream derived from gasification of oil or gas may consist of 0-30%  $\text{CO}_2$ , 10-60%  $\text{CO}$ , 25-75%  $\text{H}_2$  and 0-20%  $\text{CH}_4$  (on a dry basis). Catalysts for the above processes must exhibit the desirable properties of good activity at low temperatures, structural stability at high temperatures, resistance to deactivation by coking (relevant to the situation where the gas stream is derived from a gasification reaction) and

resistance to poisoning by sulfur compounds. The most common catalysts in use are based upon nickel supported on alumina prepared by a co-precipitation method. The use of additives to this catalyst system is also known. For instance, European Patent No 0 044 117 discloses the benefits of inclusion of magnesium in the nickel/alumina structure and also indicates the incorporation of lanthanum is beneficial in dispersing the nickel component. The amount of lanthanum added is, however, significantly less than the amount of nickel present.

The use of catalysts including nickel (or cobalt) and a noble metal, together with a rare earth oxide, has been described previously by Inui and co-workers (T. Inui *et al.*, *J. Chem. Soc. Faraday Trans. I*, **75**, 787 (1979), *J.E.C. Res.*, **28**, 427 (1989), *J.E.C. Res.*, **28**, 1285 (1989), *Stud. Surf Sci. Catal.*, **17**, 181 (1983)). The catalysts described all include a minor amount, compared to the amount of nickel, of the rare earth oxide, and further include a noble metal such as rhodium or ruthenium.

Methanation catalysts which are not based on nickel or cobalt, but instead include a noble metal such as ruthenium, rhodium or platinum, are also known.

However, the catalysts which have been described in the prior art all suffer from one or more disadvantages. For example, catalysts containing noble metals suffer from the disadvantage that they are expensive and the noble metal may be in short supply. Furthermore, some catalysts of the prior art do not exhibit particularly high activity in the conversion of carbon oxides and hydrogen to methane and/or other hydrocarbons, and many catalysts of the prior art tend to deactivate after a relatively short time owing to "coking": the formation of deposits of carbon on the surface of the catalyst.

Hence, there is a need for an improved nickel-containing catalyst which has sufficiently high activity to be of practical use in catalysis of the methanation reaction, and which is relatively resistant to coking during the reaction leading to loss of activity. It is an object of the present invention to provide a nickel-containing catalyst for use in the catalytic conversion of carbon dioxide and/or carbon monoxide to methane and/or other hydrocarbons which ameliorates at least one of the disadvantages of the nickel containing methanation catalysts which were known prior to the present invention.

Surprisingly, the present inventors have discovered that a catalyst which includes nickel and at least an equal amount by weight of one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites is effective in a process for the conversion of carbon dioxide and/or carbon monoxide to

methane and/or other hydrocarbons and has an enhanced lifetime compared to nickel containing catalysts which have hitherto been used in such a process.

### Summary of the Invention

Thus, in a first embodiment, the invention provides a process for producing a hydrocarbon product which includes the step of contacting a gaseous mixture including hydrogen and one or more oxides of carbon with a methanation catalyst at a temperature and pressure, wherein the catalyst includes:

(i) an amount of nickel sufficient for the methanation catalyst to be capable of reducing at least part of the oxide or oxides of carbon to the hydrocarbon product at the temperature and pressure and

(ii) at least an equal weight, based on the weight of nickel, of one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites.

Reference herein to a catalyst capable of at least partially reducing, or converting, an oxide of carbon to a hydrocarbon product is, as will be readily apparent to a person of ordinary skill in the relevant art, a reference to a catalyst which is capable of catalysing the reaction of an oxide of carbon with hydrogen to produce a hydrocarbon product under some conditions of temperature and pressure. That is, in the presence of such a catalyst an oxide of carbon is reduced to a hydrocarbon product under appropriate conditions of temperature and pressure at a greater rate than would occur in the absence of the catalyst under the same conditions.

The invention also relates to precursors to a catalyst for use in a process of the first embodiment. Such precursors include one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites and an amount of nickel oxide such that, after reduction of the nickel oxide in the precursor to nickel metal so as to provide a methanation catalyst, the amount of refractory oxide or oxides in the methanation catalyst is at least equal to the weight of nickel in the methanation catalyst. For example, if the desired methanation catalyst consists of a rare earth oxide and 30% by weight, based on the total weight of the catalyst, of nickel, then the catalyst precursor will include about 35% by weight, based on the total weight of the catalyst precursor, of nickel oxide, with the balance made up of the refractory oxide or oxides.

Thus, according to a second embodiment of the invention, there is provided a catalyst precursor which includes one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites and an amount of

nickel oxide sufficient for a catalyst obtainable by reducing the nickel oxide in the catalyst precursor to be capable of at least partially reducing an oxide of carbon to a hydrocarbon product, wherein the amount of refractory oxide or oxides in the methanation catalyst is at least equal to the weight of nickel in the methanation catalyst.

5 In one form of the catalyst precursor, the nickel oxide, at least in part, forms a solid solution with the refractory oxide or oxides.

Thus, according to a related second embodiment of the invention, there is provided a catalyst precursor which includes one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites and an  
10 amount of nickel oxide sufficient for a catalyst obtainable by reducing the nickel oxide in the catalyst precursor to be capable of at least partially reducing an oxide of carbon to a hydrocarbon product, wherein at least part of the nickel oxide forms a solid solution with the refractory oxide or oxides and wherein the amount of refractory oxide or oxides in the methanation catalyst is at least equal to the weight of nickel in the methanation catalyst.

15 According to a third embodiment of the invention, there is provided a process for preparing a catalyst precursor including the steps of

(i) impregnating a support material selected from the group consisting of rare earth oxides and rare earth-containing perovskites with a solution of a nickel compound so that the weight of nickel impregnated in the support material is not greater  
20 than the support material;

(ii) heating the impregnated support material at a temperature and for a time sufficient to convert the nickel compound to nickel oxide and

(iii) heating the support material at a temperature and for a time sufficient for at least part of the nickel oxide to form a solid solution with the support material.

25 The catalysts for use in the process of the first embodiment of the invention may also include one or more additives.

Therefore, in a fourth embodiment of the invention there is provided a methanation catalyst which includes

(i) an amount of nickel sufficient for the methanation catalyst to be capable  
30 of at least partially converting, in the presence of hydrogen, an oxide carbon to a hydrocarbon product at a temperature and pressure,

(ii) at least an equal weight, based on the weight of nickel, of one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites and



(iii) one or more additives selected from the group consisting of:

(a) noble metals selected from the group consisting of Pt, Ir, Rh, Ru, Os, Pd and Re;

(b) oxides selected from the group consisting of  $\text{TiO}_2$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{ZrO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Sc}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ ;

(c) oxides of elements selected from the group consisting of boron, aluminium, gallium and indium;

(d) elements selected from the group consisting of Ag, Cu, Au and Zn; and

(e) elements selected from the group consisting of P, Sb, As, Sn and Ge.

The invention further provides a catalyst precursor containing nickel oxide and capable of being converted to a methanation catalyst of the fourth embodiment by contacting the catalyst precursor with a reducing gas at an elevated temperature and for a time sufficient to reduce at least part of the nickel oxide to nickel metal.

In a fifth embodiment, the invention provides a catalyst precursor produced by the process of the third embodiment.

The invention also provides in a sixth embodiment, a methanation catalyst which is obtainable from a catalyst precursor of the second or fifth embodiments by contacting the catalyst precursor with a reducing gas at an elevated temperature and for a time sufficient to reduce at least part of the nickel oxide to nickel metal.

According to a seventh embodiment of the invention, there is provided a process for preparing a catalyst precursor including the steps of

(i) impregnating a support material selected from the group consisting of rare earth oxides and rare earth-containing perovskites with a solution of a nickel compound so that the weight of nickel impregnated in the support material is not greater than the support material;

(ii) heating the impregnated support material at a temperature and for a time sufficient to convert the nickel compound to nickel oxide and

(iii) heating the support material at a temperature and for a time sufficient for at least part of the nickel oxide to form the catalyst precursor.

In an eighth embodiment, the invention provides a catalyst precursor produced by the process of the seventh embodiment.

The invention also provides in a ninth embodiment a methanation catalyst which is obtainable from a catalyst precursor of the eighth embodiment by contacting the

catalyst precursor with a reducing gas at an elevated temperature and for a time sufficient to reduce at least part of the nickel oxide to nickel metal.

The invention also relates to precursors to a catalyst for use in a process of the first embodiment. Thus, according to a tenth embodiment of the invention, there is provided a catalyst precursor which includes one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites, said precursor including nickel or nickel cations sufficient for a catalyst obtainable by reducing the catalyst precursor to be capable of at least partially reducing an oxide of carbon to a hydrocarbon product.

In one form of the catalyst precursor, the nickel oxide, at least in part, forms a solid solution with the refractory oxide or oxides.

Thus, according to a related tenth embodiment of the invention, there is provided a catalyst precursor which includes one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites, said precursor including nickel or nickel cations sufficient for a catalyst obtainable by reducing the nickel oxide in the catalyst precursor to be capable of at least partially reducing an oxide of carbon to a hydrocarbon product, wherein at least part of the nickel oxide forms a solid solution with the refractory oxide or oxides.

According to an eleventh embodiment of the invention, there is provided a process for preparing a catalyst precursor including the steps of

(i) impregnating a support material selected from the group consisting of rare earth oxides and rare earth-containing perovskites with a solution of a nickel compound so that the weight of nickel impregnated in the support material is not greater than the support material;

(ii) if necessary, heating the impregnated support material at an atmosphere and at a temperature and for a time sufficient to convert the nickel compound to nickel oxide and

(iii) heating the support material at a temperature and for a time sufficient for at least part of the nickel oxide to form a solid solution with the support material.

In a twelfth embodiment, the invention provides a catalyst precursor produced by the process of the eleventh embodiment.

The invention also provides in a thirteenth embodiment, a methanation catalyst which is obtainable from a catalyst precursor of the twelfth embodiments by contacting

the catalyst precursor with a reducing gas at an elevated temperature and for a time sufficient to reduce at least part of the nickel oxide to nickel metal.

According to a fourteenth embodiment of the invention, there is provided a process for preparing a catalyst precursor including the steps of

(i) impregnating a support material selected from the group consisting of rare earth oxides and rare earth-containing perovskites with a solution of a nickel compound so that the weight of nickel impregnated in the support material is not greater than the support material;

(ii) if necessary, heating the impregnated support material at an atmosphere and at a temperature and for a time sufficient to convert the nickel compound to nickel oxide and

(iii) heating the support material at a temperature and for a time sufficient to form the catalyst precursor.

In a fifteenth embodiment, the invention provides a catalyst precursor produced by the process of the fourteenth embodiment.

The invention also provides in a sixteenth embodiment a methanation catalyst which is obtainable from a catalyst precursor of the fifteenth embodiment by contacting the catalyst precursor with a reducing gas at an elevated temperature and for a time sufficient to at least partially reduce the catalyst precursor and form the methanation catalyst.

### Brief Description of the Drawings

Fig. 1 is a diagrammatic representation of a Closed Loop thermochemical heat pipe.

Fig. 2 is a diagrammatic representation of an Open Loop thermochemical heat pipe.

Fig. 3 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 30 wt % Ni on yttrium oxide catalyst as a function of reaction temperature.

Figs. 4(a) to 4(c) are XRD traces for nickel oxide/yttrium oxide catalyst precursors including 0, 5 and 30 wt% nickel. respectively.

Fig. 5 includes XRD traces for nickel oxide/silica catalyst precursors, not in accordance with the present invention. having three different weight loadings of nickel.

Fig. 6 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 30 wt% Ni on terbium oxide catalyst as a function of reaction temperature.

Fig. 7 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 30 wt% Ni on terbium oxide catalyst as a function of reaction time.

Figs. 8(a) to 8(c) are XRD traces for nickel oxide/terbium oxide catalyst precursors including 0, 5 and 30 wt% nickel, respectively.

Fig. 9 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 30 wt% Ni on praseodymium oxide catalyst as a function of reaction temperature.

Figs. 10(a) to 10(c) are XRD traces for nickel oxide/praseodymium oxide catalyst precursors including 0, 5 and 30 wt% nickel, respectively.

Fig. 11 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 30 wt% Ni on samarium oxide catalyst as a function of reaction temperature.

Fig. 12 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 30 wt% Ni on samarium oxide catalyst as a function of reaction time.

Fig. 13 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 5 wt% Ni on samarium oxide catalyst as a function of reaction temperature.

Fig. 14 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 30 wt% Ni on high area yttrium oxide catalyst as a function of reaction temperature.

Figs. 15(a) to 15(c) are XRD traces for nickel oxide/high area yttrium oxide catalyst precursors including 0, 5 and 30 wt% nickel, respectively.

Fig. 16 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 30 wt% Ni on high surface area yttrium oxide catalyst as a function of reaction time.

Fig. 17 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a 5 wt% Ni on lanthanum strontium gallium magnesium oxide catalyst as a function of reaction temperature.

Fig. 18 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a prior art 10 wt% Ni on silica catalyst as a function of reaction temperature.

Fig. 19 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a prior art 30 wt% Ni on silica catalyst as a function of reaction temperature.

Fig. 20 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a prior art 4 wt% Ru on silica catalyst as a function of reaction temperature.

Fig. 21 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a prior art 30 wt% Ni on magnesium oxide catalyst as a function of reaction temperature.

Fig. 22 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a prior art 20 wt% Ni on magnesium-aluminium oxide catalyst as a function of reaction temperature.

Fig. 23 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a prior art 20 wt% Ni and 25 wt% MoO<sub>3</sub> on magnesium-aluminium oxide catalyst as a function of reaction temperature.

Fig. 24 is a graph showing the relationship between the concentration of methane, carbon monoxide, carbon dioxide and hydrogen in the presence of a prior art coprecipitated nickel-lanthanum-aluminium oxide catalyst as a function of reaction temperature.

### Detailed Description of the Invention

Usually, in the process of the first embodiment, the hydrocarbon product is methane, or methane and one or more other hydrocarbons, such as ethane, propane and butane.

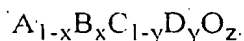
Typically, the amount of nickel in the methanation catalyst for use in the process of the first embodiment, and in a methanation catalyst obtainable by reducing the nickel oxide in a catalyst precursor of the second embodiment to nickel metal, and in the catalyst of the fourth embodiment, is in the range of from about 1% to 50% by weight, more typically from about 5% to about 40% by weight, or from about 6% to about 40% by weight, or from about 7% to about 40% by weight, or from about 8% to about 40% by weight, or from about 9% to about 40% by weight, still more typically from about 10% to about

40% by weight, even more typically from about 10% to about 30% by weight, based on the total weight of the catalyst.

As used herein, the expression "rare earth" means an element selected from yttrium, uranium and the elements of atomic number 57 to 71 inclusive.

Typically, an oxide of a rare earth metal included in the catalyst for use in the process of the first embodiment, and in a catalyst precursor of the second embodiment and a catalyst of the fourth embodiment, is selected from the group consisting of terbium oxide, erbium oxide, praseodymium oxide, samarium oxide, yttrium oxide, ytterbium oxide, lanthanum oxide, dysprosium oxide, cerium oxide, neodymium oxide, europium oxide, holmium oxide, lutetium oxide, thulium oxide and gadolinium oxide. More typically, the rare earth oxide is selected from the group consisting of terbium oxide, praseodymium oxide, samarium oxide and yttrium oxide.

A rare earth-containing perovskite for inclusion in the catalyst for use in the process of the first embodiment, and in a catalyst precursor of the second embodiment and a catalyst of the fourth embodiment is typically a substance of the general formula



wherein A is one or more lanthanide elements;

B is a metal from Group II of the Periodic Table of the Elements;

C and D are independently selected from metals of Groups IIA, IIIA, IVB, VB, VIB, VIIB and VIII of the Periodic Table of the Elements;

$$0 \leq x < 0.5;$$

$$0 \leq y \leq 1; \text{ and}$$

z is  $3-(x/2)-\delta$ , wherein  $\delta$  is an oxygen deficiency amount.

Typically, B is an alkaline earth metal selected from Mg, Ca, Sr and Ba.

Typically, C and D are independently selected from Fe, Co, Ni, Ru, Rh, Pt, Mg, Ca, Ba, Ti, Zr, V, Nb, Ta, Cr, Mo, Mn, Al, Ga and In.

Examples of rare earth-containing perovskites include perovskites of the formula  $M_{1-x}X_xYO_{3-x/2}$  or  $MYO_3$ , where M is a lanthanide, X is an alkaline earth metal and Y is a metal from Group VIII of the Periodic Table of the Elements;  $MYO_3$  where M is a lanthanide and Y is a metal from Group IVB or VIB of the Periodic Table of the Elements;  $M_{1-x}X_xY^1_{1-y}Y^2_yO_{3-x/2}$  where M is a lanthanide, X is an alkaline earth metal and  $Y^1$  and  $Y^2$  are different metals from Group IVB, VIB, VIIB or VIII of the Periodic Table of the Elements; and  $MXO_3$  where M is a lanthanide and X is a metal from Group IIIA of the Periodic Table of the Elements. More specific examples of rare earth-containing

perovskites include  $\text{MMn}_{0.5}\text{Y}_{0.5}\text{O}_3$  and  $\text{MYO}_3$  where Y is Fe, Co or Ni,  $\text{MTiO}_3$ ,  $\text{MCrO}_3$ ,  $\text{MRuO}_3$ ,  $\text{MgAlO}_3$ ,  $\text{MRhO}_3$ ,  $\text{M}_{1-x}\text{Sr}_x\text{MnO}_3$ ,  $\text{M}_{1-x}\text{Ca}_x\text{MnO}_3$ ,  $\text{M}_{1-x}\text{Sr}_x\text{YO}_3$  and  $\text{M}_{1-x}\text{Ca}_x\text{YO}_3$  where Y is Fe, Co or Ni,  $\text{M}_{1-x}\text{Sr}_x\text{AlO}_3$  and  $\text{M}_{1-x}\text{Ca}_x\text{AlO}_3$  where in each case M is a lanthanide such as lanthanum, neodymium, cerium, gadolinium, ytterbium or samarium. Still more specific examples include lanthanum-containing perovskites such as lanthanum-strontium-gallium-magnesium oxides, for example  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-z}$  or  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-z}$ ,  $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ ,  $\text{LaCoO}_3$ ,  $\text{LaNiO}_3$ ,  $\text{LaFeO}_3$ ,  $\text{LaMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ ,  $\text{LaTi}_{0.5}\text{Fe}_{0.5}\text{O}_3$ ,  $\text{LaRu}_{0.5}\text{Fe}_{0.5}\text{O}_3$ ,  $\text{LaRu}_{0.5}\text{Ni}_{0.5}\text{O}_3$ ,  $\text{LaFe}_{1-y}\text{Ni}_y\text{O}_3$ ,  $\text{LaGaO}_3$ ,  $\text{LaBaO}_3$ ,  $\text{LaMnO}_3$ ,  $\text{LaTiO}_3$ ,  $\text{LaCrO}_3$ ,  $\text{LaRuO}_3$ ,  $\text{LaRhO}_3$ ,  $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-z}$ ,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-z}$ ,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-x/2}$ ,  $\text{La}_{1-x}\text{Sr}_x\text{NiO}_{3-x/2}$ ,  $\text{La}_{0.9}\text{Ca}_{0.1}\text{AlO}_{3-z}$ ,  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-z}$  and  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-z}$  and the like, and similar substances in which the lanthanum is replaced, at least partially, with cerium, neodymium, ytterbium, europium, praseodymium, gadolinium, samarium, terbium, erbium, praseodymium, dysprosium, holmium or thulium.

The rare earth-containing perovskite is typically an oxygen ion conductor at an elevated temperature. Examples of such perovskites include  $\text{CeBaO}_3$ ,  $\text{Tb}_{0.9}\text{In}_{0.1}\text{BaO}_3$ ,  $\text{Ce}_{0.9}\text{Er}_{0.1}\text{CaO}_3$ ,  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{CaO}_3$ ,  $\text{Gd}_2\text{CeBa}_3\text{O}_8$ ,  $\text{NdAlO}_3$ ,  $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{AlO}_3$ ,  $\text{Ce}_{1-x}\text{Gd}_x\text{BaO}_{3-x}$ ,  $\text{LaGaO}_3$ ,  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-z}$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-z}$ .

Where an additive is included in the catalyst precursor or the catalyst, the amounts included are typically in the range of:

(a) for noble metals selected from the group consisting of Pt, Ir, Rh, Ru, Os, Pd and Re, from 0.01% to 20%;

(b) for oxides selected from the group consisting of  $\text{TiO}_2$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{ZrO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Sc}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ , from 0.01% to 20%;

(c) for oxides of elements selected from the group consisting of boron, aluminium, gallium and indium, from 0.01% to 20%;

(d) for elements selected from the group consisting of Ag, Cu, Au and Zn, from 0.01% to 20%; and

(e) for elements selected from the group consisting of P, Sb, As, Sn and Ge, from 0.01% to 20%;

wherein the percentages are expressed as percentages by weight based on the total weight of the catalyst.

If desired, the catalyst components may be dispersed on the surface of a support material of high surface area, such as alumina, silica, zirconia, thoria, clay, or derivatives

of clay etc. or mixtures thereof such as silica-alumina, which may provide greater structural stability to the catalyst. Formation of a supported catalyst of this kind may readily be achieved by impregnation of soluble precursors of nickel, rare earth etc on the support of choice, followed by drying and calcination. Alternatively, the catalyst components may be mixed with a material such as alumina, zirconia, clay or derivatives of clay to provide mechanical strength or increase the dispersion of the catalyst components.

The process of the first embodiment may be carried out under conditions generally known for catalytic methanation processes. The process may be carried out at atmospheric pressure, or at elevated or reduced pressure. Typically, the pressure of the gaseous mixture of hydrogen and one or more oxides of carbon is from atmospheric to about 10 MPa, more typically from atmospheric to about 1 MPa, still more typically from 100kPa to 500kPa. In a convenient form of the process of the invention, it is carried out at atmospheric pressure.

In the process of the third, seventh, eleventh or fourteenth embodiments, the heating temperature in step (ii) is typically carried out in an oxygen containing atmosphere. More typically the atmosphere is air or oxygen gas.

The process of the first embodiment may be carried out at ambient temperature or at elevated temperature, but is typically carried out at an elevated temperature, such as from about 150°C to about 1000°C, more typically from 250°C to 550°C. The contact time of the catalyst with the gaseous mixture is sufficient for at least a part of the oxide(s) of carbon to be converted to methane or other hydrocarbon(s). Typically, the gaseous mixture is passed as a flowing stream over or through a bed of the catalyst so as to provide a gas hourly space velocity (GHSV) of from about 100h<sup>-1</sup> to about 250000 h<sup>-1</sup>, more typically about 1000h<sup>-1</sup> to about 100000h<sup>-1</sup>.

The gaseous mixture may contain gases other than hydrogen and one or more oxides of carbon. For example it may contain substantially inert gases such as nitrogen, helium and/or argon, and/or one or more hydrocarbons such as methane, ethane, etc, and/or small amounts of oxygen.

Generally, the proportion of hydrogen relative to the amount of oxide(s) of carbon will be sufficient to provide at least a stoichiometric amount as calculated according to equations (1) to (3) above. However, gas compositions which include less than a stoichiometric amount of hydrogen may be used. For example, the molar ratio of H<sub>2</sub>/(CO + CO<sub>2</sub>) may be in the range of from 1:20 to 20:1, and is more usually in the range



of from 1:2 to 10:1, still more usually in the range of from 1:1 to 5:1, such as from 1:1 to 4.5:1 or 1:1 to 4.3:1 or 1:1 to 4.1:1 or 1:1 to 4.0:1 or 1:1 to 3.9:1 or 1:1 to 3.8:1 or 1:1 to 3.7:1 or 1:1 to 3.6:1 or 1:1 to 3.5:1 or 1:1 to 3.4:1 or 1:1 to 3.3:1 or 1:1 to 3.2:1 or 1:1 to 3.1:1 or 1:1 to 3:1 or 1:1 to 2.9:1 or 1:1 to 2.8:1 or 1:1 to 2.7:1 or 1:1 to 2.6:1 or 1:1 to 2.5:1 or 1:1 to 2.4:1 or 1:1 to 2.3:1 or 1:1 to 2.2:1 or 1:1 to 2.1:1 or 1:1 to 2.0:1.

The catalysts for use in the process of the first embodiment may be prepared using techniques which are generally known in the art. For example, the catalyst precursor may be prepared by conventional wet impregnation of the refractory oxide or oxides. In such a process, and in a process of the third embodiment, the support material may be impregnated with an aqueous solution of a water-soluble nickel salt, such as nickel nitrate, which is capable of being converted *in situ* to nickel oxide, for example by the application of heat, or oxidising in an oxidising atmosphere. Alternatively, a nickel salt which is soluble in a non-aqueous solvent can be used, in which case it will be appreciated that the impregnating will be carried out using a non-aqueous solvent. After impregnation, the impregnated support material is typically calcined in air at a temperature in the range selected from the group consisting of from 250°C to 1500°C, 250°C to 1400°C, 250°C to 1300°C, 250°C to 1200°C, 250°C to 1100°C, 250°C to 1000°C, 250°C to 900°C, 300°C to 900°C, more typically 250°C to 800°C, and still more typically in the range of 350 to 600°C to convert the impregnated nickel salt to nickel oxide.

The preparation method for the catalyst precursor of a methanation catalyst for use in the process of the first embodiment is however not restricted to wet impregnation techniques, and alternative synthesis routes known to those skilled in the art can also be employed, examples of which include co-precipitation, solid state reaction, vapor phase deposition etc.

In one form of the present invention, the methanation catalyst includes a rare earth oxide which has been prepared so as to possess an enhanced surface area, compared to commercially available rare earth oxides. A process for preparing such a rare earth oxide typically includes the steps of dissolving a commercially available rare earth oxide in an excess of an acid, usually nitric acid, followed by the addition of sufficient of a precipitating anion to substantially completely precipitate the rare earth as an insoluble salt at an appropriate pH. The resulting insoluble salt is then dried under controlled conditions, such as by spray drying, to minimise compaction of the powder. The insoluble salt is next fired to decompose it to the corresponding oxide. The

decomposition pathway of a sample of the insoluble salt is first monitored by thermal analysis such as differential thermal analysis (DTA), thermogravimetric analysis (TGA) and/or differential scanning calorimetry (DSC). From the observed decomposition profile, a firing procedure is determined which minimises formation of undesirable intermediates.

In many instances, the precipitant is suitably a dicarboxylic acid or one or more derivatives thereof. The derivatives may include salts, esters, anhydrides, amides and the like. Ammonium oxalate is one suitable derivative. Dimethyl oxalate or diethyl oxalate are also suitable. A suitable dicarboxylic acid is oxalic acid. Another suitable solution of precipitant is an aqueous solution of tartaric acid. A solution of ammonium carbonate as well as ammonia can also be used as a solution of precipitant.

Also suitable as precipitants are aqueous solutions of sodium carbonate or potassium carbonate. An example of such a solution of coprecipitating ions is an aqueous solution of hydroxide and carbonate ions such as a solution of an alkylammonium hydroxide and carbonate ions together with oxalic acid or derivatives of oxalic acid.

Typically, an alkaline solution of an oxalate is used as a solution of coprecipitating ions, such as an aqueous solution of sodium hydroxide or potassium hydroxide and oxalic acid or derivatives of oxalic acid.

Another suitable precipitant is an aqueous solution of ammonium polyacrylate, which when mixed with the solution of rare earth metal ions results in rare earth metal polyacrylate precipitates.

The solution of precipitant may typically include a pH adjusting agent in order that the pH can be adjusted to maximise precipitation. An aqueous solution of triethanolamine and oxalic acid in a molar ratio of about 1 to about 3, or about 1 to about 2.5 or about 1.8 to about 2.2 is one such example. Alternatively, an aqueous solution of oxalic acid and urea is envisaged as a solution of precipitating ions with urea acting as a solvent to control pH.

An organic solvent miscible with water can be used to make the solution of precipitating ions. Typically organic solvents such as methanol, ethanol, propanol, butanol, pentanol, hexanol or acetone can be used to make a solution of precipitating ions such as an oxalic acid solution.

It will be appreciated that where the catalyst precursor includes more than one rare earth oxide, a mixture of rare earth oxides may be obtained by a procedure

substantially as described above, by co-precipitating insoluble salts of the rare earth elements.

After the insoluble rare earth metal salt is obtained and dried, it is fired to produce the corresponding oxide.

5           The catalyst for the process of the first embodiment of the invention is produced by reduction of a catalyst precursor, including but not limited to a catalyst precursor of the second embodiments, or a catalyst precursor produced according to the process of the third or seventh embodiments or a precursor of the methanation catalyst of the fourth embodiment. This reduction may be achieved either concomitantly with or immediately  
10       prior to the methanation reaction as a result of contacting the catalyst precursor with the reactant gaseous mixture of hydrogen and carbon oxide(s), or more typically, the reduction may be carried out by pre-reducing the catalyst at a temperature of 300°C or greater with a gas stream consisting at least predominantly of hydrogen or any other readily available gaseous reductant such as carbon monoxide, methane and/or other  
15       hydrocarbons, or mixtures of the foregoing. In the case of reduction of the catalyst precursor by contacting it with the reactant gaseous mixture, the catalyst precursor temperature is typically raised to a temperature in excess of 500°C until the precursor is substantially completely reduced. For some catalyst compositions, the precursor may be reduced at a temperature as low as 300°C, although a temperature in excess of 500°C is  
20       more typical. Other catalyst precursor compositions may require reduction at still higher temperatures, such as up to about 900°C. Without wishing to be bound by theory, it is speculated by the present inventors that in a catalyst precursor composition of the second embodiment it is necessary to partially reduce a fraction of the nickel ions present in the solid solution to produce small metal crystallites which participate in the catalytic  
25       reaction. Therefore, the reduction procedure employed should preferably be at a temperature which will facilitate reduction of a fraction of the nickel ions to nickel metal. Given the teaching herein, it is a matter of no more than routine experimentation to establish appropriate reduction conditions to achieve this objective for any given catalyst precursor of the invention.

30           The identification of a solid solution in a catalyst precursor of the latter of the second embodiments may be made by inspection of an X-ray powder diffraction profile for the precursor. The nature of the solid solution depends to a large extent on the pre-treatment that the catalyst precursor receives prior to reduction. Parameters which influence the formation of a solid solution are calcination temperature ( $T_c$ ), calcination

time ( $t_c$ ) and nickel loading. In general, the calcination temperature, that is, the temperature used in step (iii) of the process of the third embodiment is usually in the range 250 to 800°C, and is more typically in the range of 350 to 600°C.

Another feature of the catalysts of the present invention is the general observation that the catalyst surface area increases as the nickel loading increases. For example, Table 1 illustrates the surface areas as calculated by the standard BET method for several of the catalysts revealed in this disclosure, and for comparison purposes, surface areas of silica and nickel oxide/silica composites obtained by similar methods are also shown.

## EXAMPLES

### Example 1

A 30 weight % nickel/yttrium oxide catalyst was made by impregnating yttrium oxide (Pi-Kem, UK) with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at 110°C, and calcination in air at 500°C for 2 hours. The methanation activity was evaluated by contacting the catalyst with a gaseous feedstock comprising of 20% methane, 17% carbon dioxide, 30% carbon monoxide and 32% hydrogen at a flow rate sufficient to give a gas hourly space velocity (GHSV) of 10,000 h<sup>-1</sup>. The catalyst was allowed to equilibrate at specific temperatures in the range 250 to 550°C and all effluent gas concentrations were measured using an on-line gas chromatograph. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 3. Significantly, the theoretical maximum for methane formation was obtained using this catalyst at low temperature (400°C or less) conditions and moreover, no coking of the catalyst bed was detected.

Figures 4(a) to 4(c) shows X-ray diffraction (XRD) patterns for yttrium oxide, 5 wt% nickel oxide-yttrium oxide and the 30 wt% nickel oxide-yttrium oxide precursor of this Example, respectively. As seen in Figure 4(a), the XRD trace for pure yttrium oxide is very sharp and intense which is indicative, to those of ordinary skill, of a highly crystalline material. Significantly, the XRD pattern becomes less intense and the lines become broader in character as the nickel is added. Indeed the 30 wt% nickel oxide-yttrium oxide catalyst precursor exhibits extremely broad lines due to the yttrium oxide component which is recognized by those skilled in the art to be representative of an amorphous or nanocrystalline oxide material (see Fig. 4(c)). In harmony with this observation is the presence of very wide reflections attributable to nickel oxide which again not only indicates the presence of amorphous or nanocrystalline nickel oxide but

also the weak intensity of these latter features can be interpreted as meaning that there may exist a fraction of the nickel species in a solid solution with the yttrium oxide.

Inspection of comparative XRD profiles for known nickel/silica catalysts provides a clear indication of the novel and surprising behaviour of the catalysts disclosed in this invention. Figure 5 illustrates XRD profiles recorded for a series of calcined nickel/silica catalysts. The silica support is characterized by an amorphous "lump" at low values of 2-theta, whereas sharp, intense peaks are apparent for nickel oxide at 37, 43 and 63 degrees 2-theta. As the loading of nickel becomes higher, the XRD peaks become narrower, thus indicating that the nickel particles were becoming larger and more crystalline in character. Electron microscopy observations are consistent with this interpretation. Importantly, the silica support of the nickel/silica catalyst does not have the ability to form a solid solution with nickel. Consequently, the nickel particles are neither as well dispersed as in those catalysts described in this invention or as small and amorphous or nanocrystalline in structure.

### Example 2

A 30 weight% nickel/terbium oxide catalyst was made by impregnating terbium oxide (Pi-Kem, UK) with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at 110°C, and calcination in air at 500°C for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 6. Significantly, the theoretical maximum for methane formation was obtained using this catalyst at low temperature (400°C or less) conditions and moreover, no coking of the catalyst bed was detected.

The activity of the 30wt% nickel/terbium oxide catalyst was evaluated as a function of reaction time to determine not only the stability but also the extent of catalyst coking. A gaseous feed consisting of 19% methane, 17% carbon dioxide, 30% carbon monoxide and 34% hydrogen was passed over a catalyst sample at a flow rate such as to give a space velocity of 10,000 h<sup>-1</sup> and at a temperature of 400°C. A plot of the concentration of each species in the gas phase as a function of reaction time is displayed in Figure 7. Not only was the catalytic activity stable but no coke deposition was noted on the catalyst bed following reaction.

Figures 8(a) to 8(c) display XRD patterns for terbium oxide, 5 wt% nickel oxide/terbium oxide and the 30 wt% nickel oxide/terbium oxide catalyst precursor of this Example, respectively. As in the case of the nickel oxide-yttrium oxide catalyst the

features for the terbium oxide component diminish in intensity as the nickel loading is increased, again indicative of a more amorphous or nanocrystalline material. Furthermore, the reflections characteristic for nickel oxide are extremely weak in intensity in Fig. 8(c). Therefore, without wishing to be bound by theory, it appears that the nickel component may at least in part be forming a solid solution with the rare earth oxide or at least the rare earth oxide has the ability to disperse the nickel component to a greater extent, than that for a silica support.

### Example 3

A 30 weight% nickel/praseodymium oxide catalyst was made by impregnating praseodymium oxide (Pi-Kem, UK) with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at 110°C, and calcination in air at 500°C for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 9. The theoretical maximum for methane formation was obtained using this catalyst at low temperature (400°C or less) conditions and no coking of the catalyst bed was detected.

Figures 6(a) to 6(c) display XRD patterns for praseodymium oxide, 5 wt% nickel oxide/praseodymium oxide and the 30 wt% nickel oxide/praseodymium oxide catalyst precursor of this Example, respectively. The nickel oxide/praseodymium oxide system behaves similarly to the nickel oxide/yttrium oxide and nickel oxide/terbium oxide systems. The XRD traces in Figures 10(a) to 10(c) clearly illustrate that the reflections assigned to praseodymium oxide become very broad and weak in intensity as the nickel loading increases. Furthermore, there is very little evidence for the presence of nickel crystallites, thus again indicating that either a solid solution has formed or that the praseodymium oxide has a surprising ability to disperse nickel oxide particles extremely well, that is to an extent where the nickel oxide particles become amorphous or nanocrystalline.

### Example 4

A 30 weight% nickel/samarium oxide catalyst was made by impregnating samarium oxide (Pi-Kem, UK) with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at 110°C, and calcination in air at 500°C for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 11. The theoretical maximum for methane

formation was obtained using this catalyst at low temperature (400°C or less) conditions and no coking of the catalyst bed was detected.

The activity of the 30 wt% nickel/samarium oxide catalyst was evaluated as a function of reaction time to determine not only the stability but also the extent of catalyst coking. A gaseous feed consisting of 19% methane, 17% carbon dioxide, 30% carbon monoxide and 34% hydrogen was passed over a catalyst sample at a flow rate such as to give a space velocity of 10,000 h<sup>-1</sup> and at a temperature of 400°C. A plot of the concentration of each species in the gas phase as a function of reaction time is displayed in Figure 12. Not only was the catalytic activity stable but no coke deposition was noted on the catalyst bed following reaction.

#### Example 5

A 5 weight% nickel/samarium oxide catalyst was made by impregnating samarium oxide (Pi-Kem, UK) with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at 110°C, and calcination in air at 500°C for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 13. This catalyst containing only 5% nickel was very active for the methanation reaction.

#### Example 6

Commercial yttrium oxide (Pi-Kem, UK) was reprocessed by a novel material synthesis procedure to produce a material of enhanced surface area (20 m<sup>2</sup>g<sup>-1</sup>). Yttrium oxide was initially dissolved in 10 % excess nitric acid then sufficient oxalate ions were added to completely precipitate yttrium as yttrium oxalate at appropriate pH to optimise precipitation. The product was dried under controlled conditions by spray drying, to minimise compaction of powder. Following thermal analysis of the decomposition pathway, a firing procedure was determined which minimises formation of undesirable intermediates. A 30 weight% nickel/yttrium oxide catalyst was made by impregnating the high area yttrium oxide obtained in this way with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at 110°C, and calcination in air at 500°C for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 14. The low temperature methanation activity (temperature of 350°C or less) was substantially greater than that measured on a commercially available yttrium oxide support. The theoretical maximum

for methane formation was obtained using this catalyst at low temperature (400°C or less) conditions and no coking of the catalyst bed was detected.

Figures 15(a) to 15(c) shows X-ray diffraction (XRD) patterns for the high area yttrium oxide, 5 wt% nickel oxide-high area yttrium oxide and the 30 wt% nickel oxide-high area yttrium oxide precursor of this Example, respectively. As seen in Figures 15(a) to 15(c) this system behaves similarly to the nickel oxide-yttrium oxide system described in Example 1 and indicates the presence of amorphous or nanocrystalline nickel oxide and/or a fraction of the nickel species in a solid solution with the yttrium oxide, in the 30 wt% nickel oxide composition of this Example.

The activity of the 30 wt% nickel/high area yttrium oxide catalyst was evaluated as a function of reaction time to determine not only the stability but also the extent of catalyst coking. A gaseous feed consisting of 19% methane, 17% carbon dioxide, 30% carbon monoxide and 34% hydrogen was passed over a catalyst sample at a flow rate such as to give a space velocity of 10,000 h<sup>-1</sup> and at a temperature of 400°C. A plot of the concentration of each species in the gas phase as a function of reaction time is displayed in Figure 16. Not only was the catalytic activity stable but no coke deposition was noted on the catalyst bed following reaction.

### Example 7

A portion of the oxygen ion conductor lanthanum-strontium-gallium-magnesium oxide (La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-x</sub>) was impregnated with an amount of aqueous solution of nickel nitrate sufficient to give a loading of 5 wt% Ni on the oxide, followed by drying the sample at 110°C, and calcination in air at 500°C for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 17. This catalyst displayed excellent activity for methanation at relatively high temperatures (450°C or higher).

### Comparative Example 1

A 10 wt% nickel/silica catalyst was made by impregnating silica (Cab-O-Sil M5, 200 m<sup>2</sup>g<sup>-1</sup>, Cabot Corporation, Boston, Mass. U.S.A.) with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at 110°C, and calcination in air at 500°C for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 18. Visual inspection of the catalyst bed following reaction showed the presence of large black coke



particles which indicated the presence of substantial concentrations of coke which would lead to poisoning of the catalyst during industrial use.

### Comparative Example 2

A 30 wt% nickel/silica catalyst was made by impregnating silica (Cab-O-Sil M5,  $200 \text{ m}^2\text{g}^{-1}$ ) with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at  $110^\circ\text{C}$ , and calcination in air at  $500^\circ\text{C}$  for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 19. Visual inspection of the catalyst bed following reaction showed the presence of large black coke particles which indicated the presence of substantial concentrations of coke which would lead to poisoning of the catalyst during industrial use.

### Comparative Example 3

A 4 wt% ruthenium/silica catalyst was made by impregnating silica (Cab-O-Sil M5,  $200 \text{ m}^2\text{g}^{-1}$ ) with an appropriate amount of aqueous solution of ruthenium chloride, followed by drying the sample at  $110^\circ\text{C}$ , and calcination in air at  $600^\circ\text{C}$  for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 20. This catalyst did not display sufficient methanation activity under the applied conditions, in contrast to the catalysts of the present invention.

### Comparative Example 4

A 30 wt% nickel/magnesium oxide catalyst was made by impregnating commercially available magnesium oxide with an appropriate amount of aqueous solution of nickel nitrate, followed by drying the sample at  $110^\circ\text{C}$ , and calcination in air at  $500^\circ\text{C}$  for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 21. This catalyst did not display sufficient methanation activity under the applied conditions, in contrast to the catalyst of the present invention.

### Comparative Example 5

A highly heat resistant solid catalyst for methanation of hydrogen and carbon monoxide as described in US patent No. 4,331,544 was made as follows. 10.033 grams of aluminium nitrate and 5.029 grams magnesium nitrate were dissolved in 25 mL of purified water. Approximately 25 mL of ammonium hydroxide solution was added to the

aforementioned solution while under vigorous stirring in order to form a precipitate. The precipitate was filtered and washed thoroughly with distilled water and then dried at 110°C. Finally, the material was calcined in a muffle furnace in air at 500°C for 4 hours. A catalyst for evaluation was made by impregnating the magnesium oxide-aluminium oxide carrier with an appropriate amount of nickel nitrate such that the loading of nickel was 20 wt%. The catalyst was pretreated by drying at 110°C and calcination at 500°C for 2 hours. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 22. Although, the activity was reasonable, albeit not as good as that recorded for the catalysts described in this invention, coking of the catalyst bed was again noted thus this catalyst is not suitable for industrial application.

#### Comparative Example 6

A catalyst similar to that described in comparative example 5 was synthesized, the only difference being that a mixture of nickel nitrate and ammonium molybdate was impregnated on the magnesium oxide-aluminium oxide support such that the weight ratio of NiO-MoO<sub>3</sub> carrier was 20:25:55. The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 23. Significantly, this catalyst did not display sufficient methanation activity under the applied conditions in contrast to the catalyst of the present invention.

#### Comparative Example 7

A nickel containing catalyst claimed to exhibit high thermal stability and excellent resistance to carbon deposition according to EP 0 044 117 was made as follows. An aqueous solution containing 2.518 grams of lanthanum nitrate, 11.809 grams of aluminium nitrate and 22.903 grams of nickel nitrate was prepared, and to this was added under vigorous stirring a solution of sodium bicarbonate. The resultant pale green suspension was filtered and washed thoroughly with distilled water. The precipitate was dried at 110°C and then calcined in a muffle furnace at 450°C for 1 hour. The formed nickel-lanthanum-aluminium oxide catalyst had a Ni/Al atomic ratio of 2.5 and a lanthanum content of 0.05, expressed as the atomic fraction La/(Ni+Al+La). The methanation activity was evaluated in the same manner as outlined in Example 1. A plot of the concentration of each species in the gas phase as a function of reaction temperature is displayed in Figure 24. Significantly, this catalyst did not display sufficient

methanation activity under the applied conditions in contrast to the catalyst of the present invention.

**TABLE 1****BET surface areas of representative catalysts of the invention and other materials**

Catalyst composition	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
yttrium oxide	2.46
10 % Ni on yttrium oxide	15.71
30 % Ni on yttrium oxide	49.36
terbium oxide	0.76
5 % Ni on terbium oxide	5.82
30 % Ni on terbium oxide	14.51
praseodymium oxide	3.58
5 % Ni on praseodymium oxide	8.47
30 % Ni on praseodymium oxide	11.69
silica	206.28
10%Ni on silica	171.80
30 % Ni on silica	123.40

## Claims

1. A catalyst precursor which includes one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites, said precursor including nickel or nickel cations sufficient for a catalyst obtainable by reducing the catalyst precursor to be capable of at least partially reducing an oxide of carbon to a hydrocarbon product.

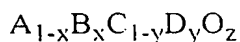
2. A catalyst precursor which includes one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites, said precursor including nickel or nickel cations sufficient for a catalyst obtainable by reducing nickel oxide in the catalyst precursor to be capable of at least partially reducing an oxide of carbon to a hydrocarbon product, wherein at least part of the nickel oxide forms a solid solution with the refractory oxide or oxides.

3. A catalyst precursor which includes one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites and an amount of nickel oxide sufficient for a catalyst obtainable by reducing the nickel oxide in the catalyst precursor to be capable of at least partially reducing an oxide of carbon to a hydrocarbon product, wherein the amount of refractory oxide or oxides in the catalyst is at least equal to the weight of nickel in the catalyst.

4. A catalyst precursor according to claim 3, wherein at least part of the nickel oxide forms a solid solution with the refractory oxide or oxides.

5. A catalyst precursor according to any one of claims 1-4 wherein the refractory oxide is a rare earth oxide selected from the group consisting of terbium oxide, erbium oxide, praseodymium oxide, samarium oxide, yttrium oxide, ytterbium oxide, lanthanum oxide, dysprosium oxide, cerium oxide, neodymium oxide, europium oxide, holmium oxide, lutetium oxide, thulium oxide and gadolinium oxide.

6. A catalyst precursor according to any one of claims 1-4 wherein the refractory oxide is a rare earth-containing perovskite of the general formula



wherein A is one or more lanthanide elements;

B is a metal from Group II of the Periodic Table of the Elements;

C and D are independently selected from metals of Groups IIA, IIIA, IVB, VB, VIB, VIIB and VIII of the Periodic Table of the Elements;

$\leq x < 0.5$ ;

$0 \leq y \leq 1$ ; and

$z$  is  $3-(x/2)-\delta$ , wherein  $\delta$  is an oxygen deficiency amount.

7. A catalyst precursor according to claim 6, wherein B is an alkaline earth metal selected from Mg, Ca, Sr and Ba.

8. A catalyst precursor according to claim 6 wherein C and D are independently selected from Fe, Co, Ni, Ru, Rh, Pt, Mg, Ca, Ba, Ti, Zr, V, Nb, Ta, Cr, Mo, Mn, Al, Ga and In.

9. A catalyst precursor according to claim 6 wherein the rare earth-containing perovskite is an oxygen ion conductor at an elevated temperature.

10. A catalyst precursor according to claim 9 wherein the rare earth containing perovskite is selected from the group consisting of  $\text{CeBaO}_3$ ,  $\text{Tb}_{0.9}\text{In}_{0.1}\text{BaO}_3$ ,  $\text{Ce}_{0.9}\text{Er}_{0.1}\text{CaO}_3$ ,  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{CaO}_3$ ,  $\text{Gd}_2\text{CeBa}_3\text{O}_8$ ,  $\text{NdAlO}_3$ ,  $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{AlO}_3$ ,  $\text{Ce}_{1-x}\text{Gd}_x\text{BaO}_{3-x}$ ,  $\text{LaGaO}_3$ ,  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-z}$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-z}$ .

11. A process for preparing a catalyst precursor including the steps of

(i) impregnating a support material selected from the group consisting of rare earth oxides and rare earth-containing perovskites with a solution of a nickel compound so that the weight of nickel impregnated in the support material is not greater than the support material;

(ii) if necessary, heating the impregnated support material in an atmosphere and at a temperature and for a time sufficient to convert the nickel compound to nickel oxide and

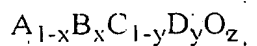
(iii) heating the support material at a temperature and for a time sufficient to form the catalyst precursor.

12. A process according to claim 11 wherein the support material is a rare earth oxide.

13. A process according to claim 12 wherein the rare earth oxide support material is prepared by dissolving a rare earth oxide in an excess of an acid, addition of sufficient of a precipitating anion to substantially completely precipitate the rare earth as an insoluble salt, drying the insoluble salt and firing the insoluble salt to decompose it to the corresponding oxide.

14. A process according to claim 11 wherein the rare earth oxide is selected from the group consisting of terbium oxide, erbium oxide, praseodymium oxide, samarium oxide, yttrium oxide, ytterbium oxide, lanthanum oxide, dysprosium oxide, cerium oxide, neodymium oxide, europium oxide, holmium oxide, lutetium oxide, thulium oxide and gadolinium oxide.

15. A process according to claim 11 wherein the support material is a rare earth-containing perovskite of the general formula



wherein A is one or more lanthanide elements;

B is a metal from Group II of the Periodic Table of the Elements;

C and D are independently selected from metals of Groups IIA, IIIA, IVB, VB, VIB, VIIB and VIII of the Periodic Table of the Elements;

$0 \leq x < 0.5$ ;

$0 \leq y \leq 1$ ; and

z is  $3-(x/2)-\delta$ , wherein  $\delta$  is an oxygen deficiency amount.

16. A process according to claim 15, wherein B is an alkaline earth metal selected from Mg, Ca, Sr and Ba.

17. A process according to claim 16 wherein C and D are independently selected from Fe, Co, Ni, Ru, Rh, Pt, Mg, Ca, Ba, Ti, Zr, V, Nb, Ta, Cr, Mo, Mn, Al, Ga and In.

18. A process according to claim 15 wherein the rare earth-containing perovskite is an oxygen ion conductor at an elevated temperature.

19. A process according to claim 18 wherein the rare earth containing perovskite is selected from the group consisting of  $CeBaO_3$ ,  $Tb_{0.9}In_{0.1}BaO_3$ ,  $Ce_{0.9}Er_{0.1}CaO_3$ ,  $Ce_{0.9}Gd_{0.1}CaO_3$ ,  $Gd_2CeBa_3O_8$ ,  $NdAlO_3$ ,  $Nd_{0.9}Ca_{0.1}AlO_3$ ,  $Ce_{1-x}Gd_xBaO_{3-x}$ ,  $LaGaO_3$ ,  $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-z}$  and  $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-z}$ .

20. A process according to any one of claims 11-19 wherein in step (iii) the heating is at a temperature and for a time sufficient for at least part of the nickel oxide to form a solid solution with the support material.

21. A catalyst precursor produced by the process of any one of claims 11-19.

22. A catalyst precursor produced by the process of claim 20.

23. A methanation catalyst which is obtainable from a catalyst precursor of any one of claims 1-4 by contacting the catalyst precursor with a reducing gas at an elevated temperature and for a time sufficient to reduce at least part of the nickel oxide to nickel metal.

24. A methanation catalyst which includes

(i) an amount of nickel sufficient for the methanation catalyst to be capable of at least partially converting, in the presence of hydrogen, an oxide carbon to a hydrocarbon product at a temperature and pressure,

(ii) at least an equal weight, based on the weight of nickel, of one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites and

(iii) one or more additives selected from the group consisting of:

(a) noble metals selected from the group consisting of Pt, Ir, Rh, Ru, Os, Pd and Re;

(b) oxides selected from the group consisting of  $\text{TiO}_2$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{ZrO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Sc}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ ;

(c) oxides of elements selected from the group consisting of boron, aluminium, gallium and indium;

(d) elements selected from the group consisting of Ag, Cu, Au and Zn; and

(e) elements selected from the group consisting of P, Sb, As, Sn and Ge.

25. A catalyst precursor containing nickel oxide and capable of being converted to a methanation catalyst according to claim 24 by contacting the catalyst precursor with a reducing gas at an elevated temperature and for a time sufficient to reduce at least part of the nickel oxide to nickel metal.

26. A process for producing a hydrocarbon product which includes the step of contacting a gaseous mixture including hydrogen and one or more oxides of carbon with a methanation catalyst at a temperature and pressure, wherein the catalyst includes:

(i) an amount of nickel sufficient for the methanation catalyst to be capable of reducing at least part of the oxide or oxides of carbon to the hydrocarbon product at the temperature and pressure and

(ii) at least an equal weight, based on the weight of nickel, of one or more refractory oxides selected from the group consisting of rare earth oxides and rare earth-containing perovskites.

27. A process for producing a hydrocarbon product which includes the step of contacting a gaseous mixture including hydrogen and one or more oxides of carbon with a methanation catalyst at a temperature and pressure, wherein the methanation catalyst is a catalyst according to claim 23.

28. A process for producing a hydrocarbon product which includes the step of contacting a gaseous mixture including hydrogen and one or more oxides of carbon



with a methanation catalyst at a temperature and pressure, wherein the methanation catalyst is a catalyst according to claim 24.

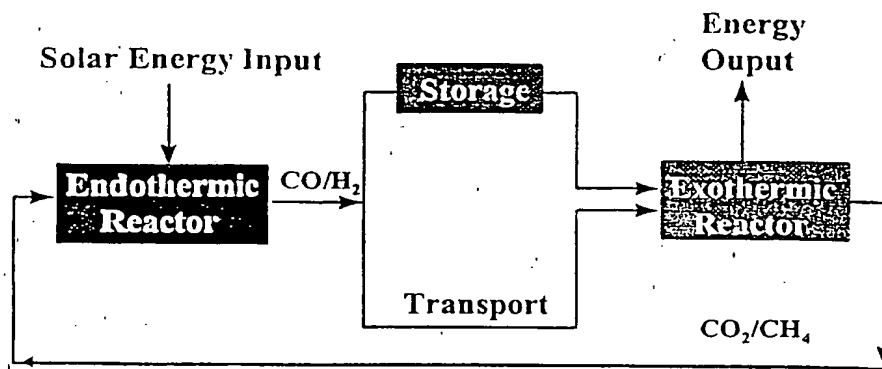


FIGURE 1

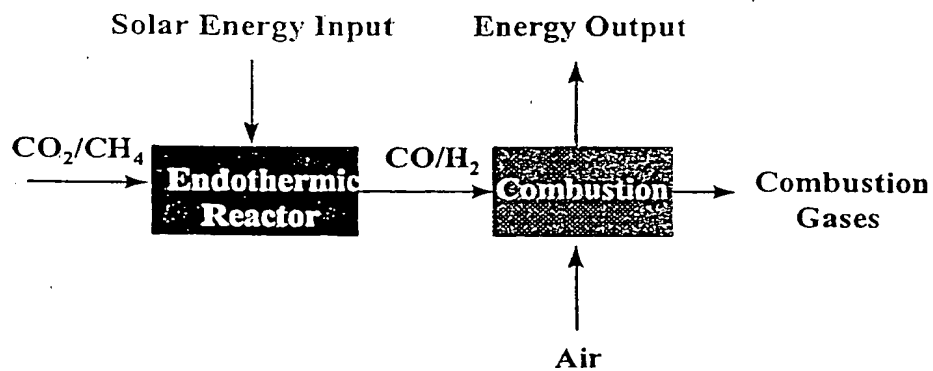
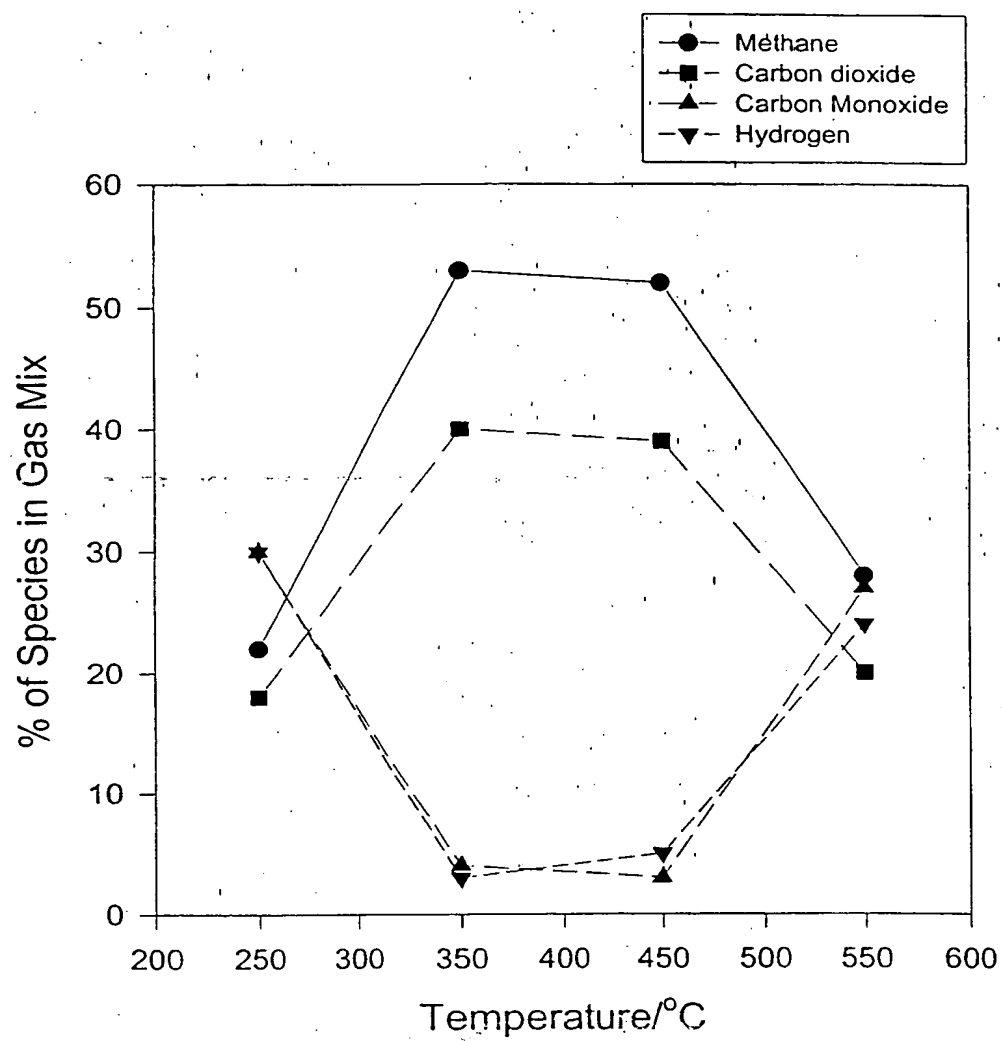
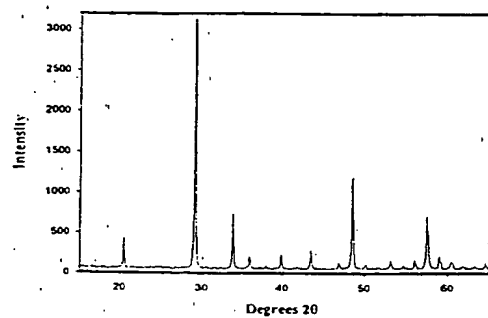


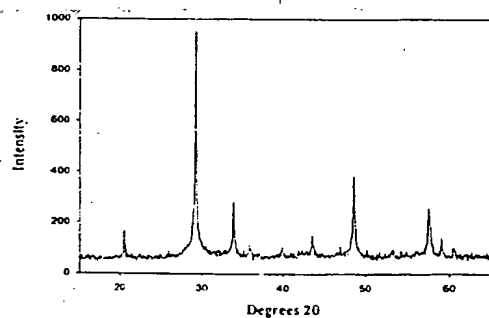
FIGURE 2

**Figure 3**



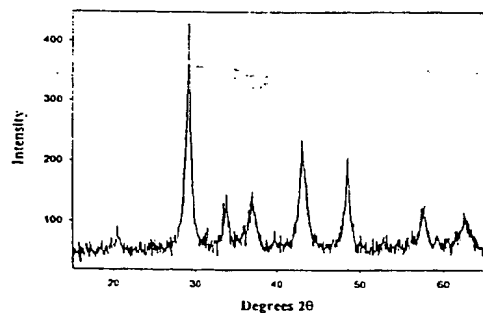
yttrium oxide

Figure 4(a)



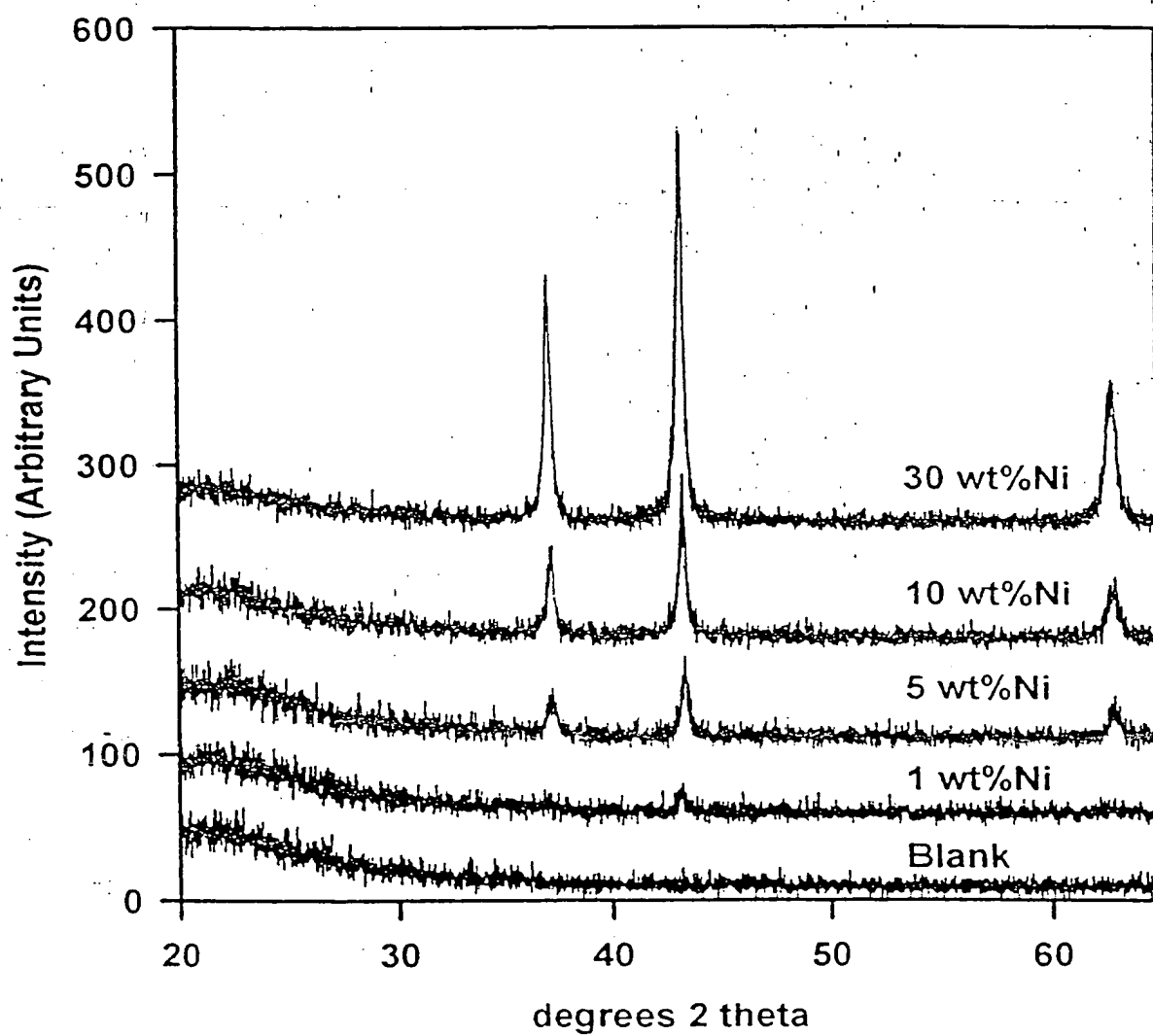
5 wt % nickel on yttrium oxide

Figure 4(b)



30 % Ni on yttrium oxide

Figure 4(c)

**Figure 5**

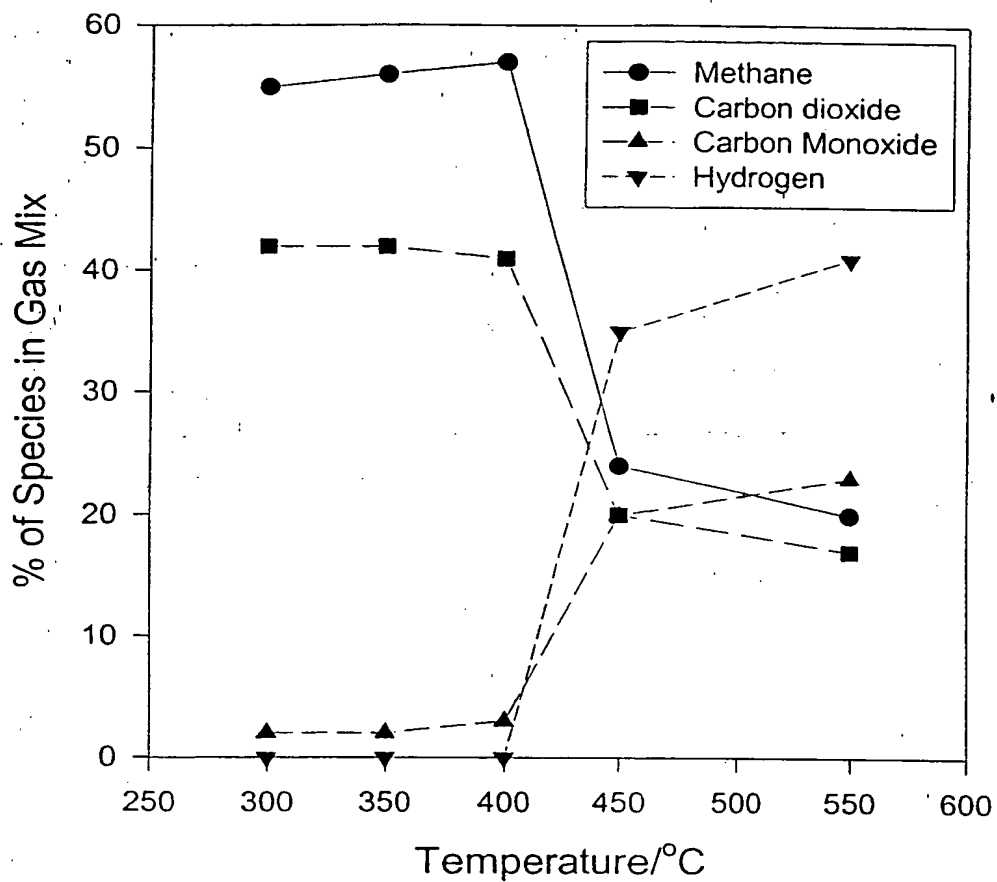
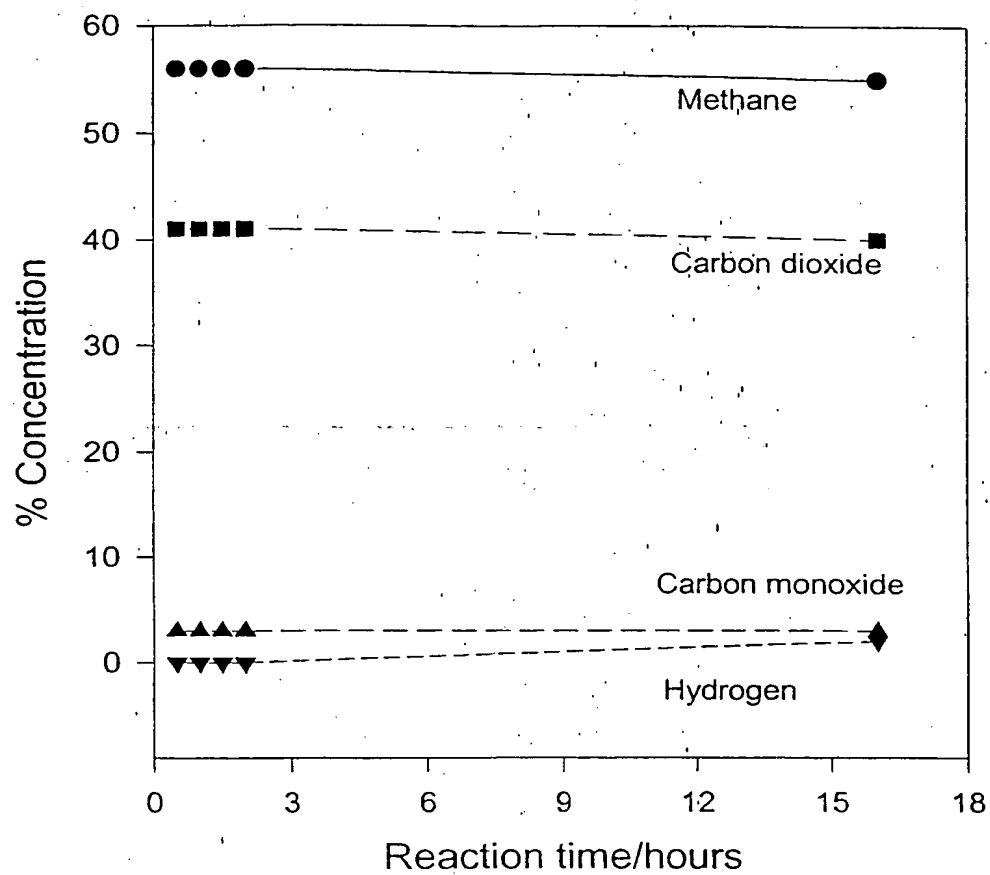
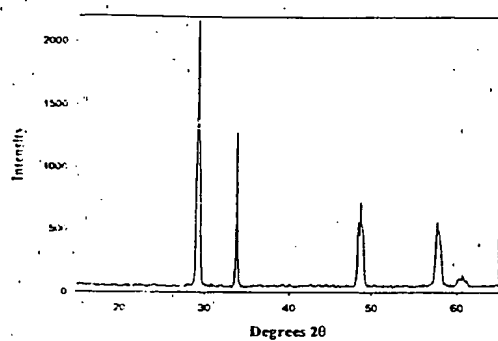


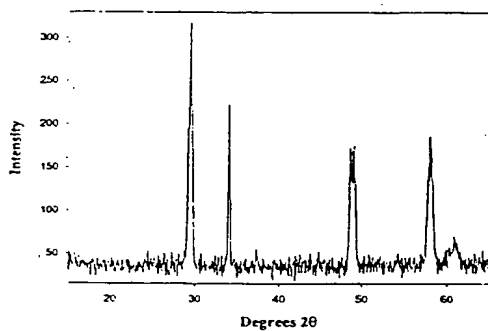
Figure 6

**Figure 7**



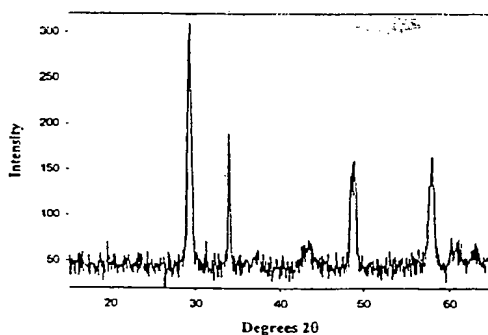
terbium oxide

Figure 8(a)



5 wt % Ni on terbium oxide

Figure 8(b)



30 % Ni on terbium oxide

Figure 8(c)



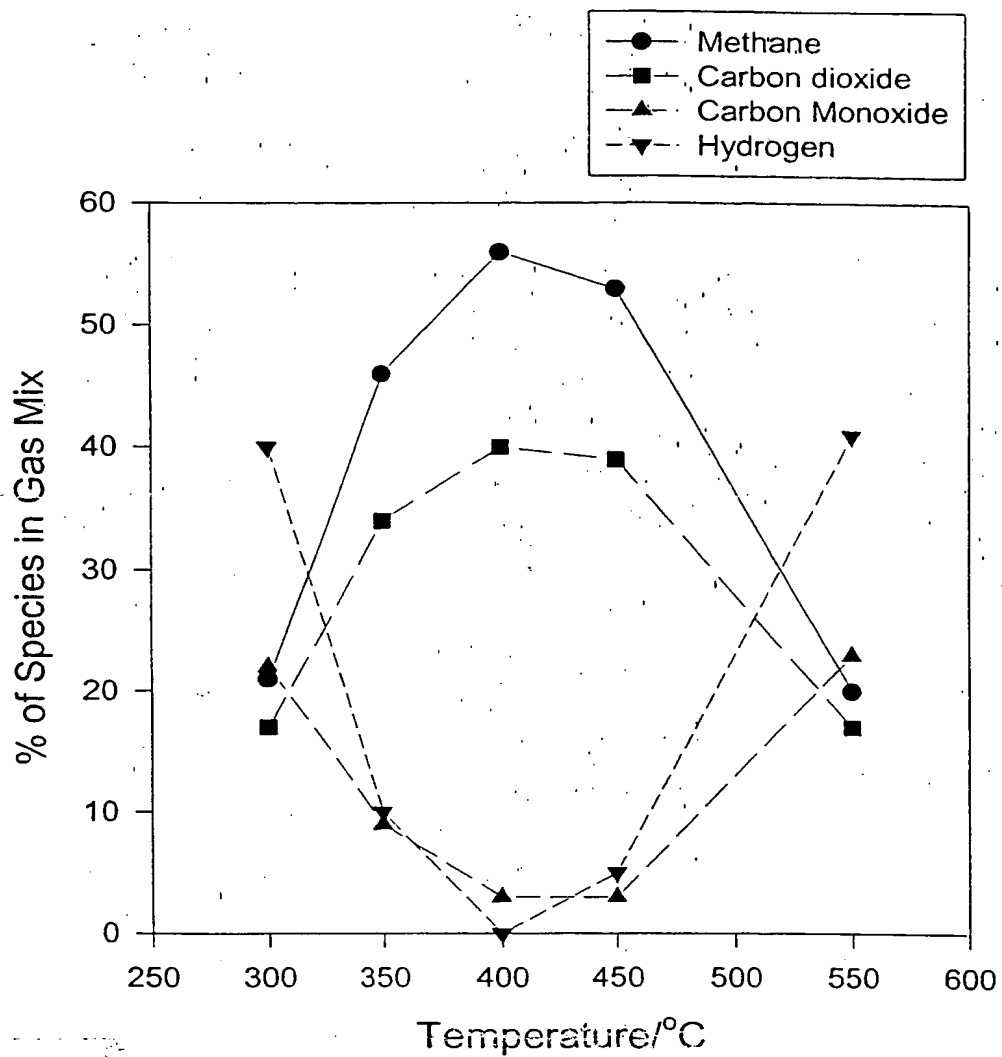


Figure 9

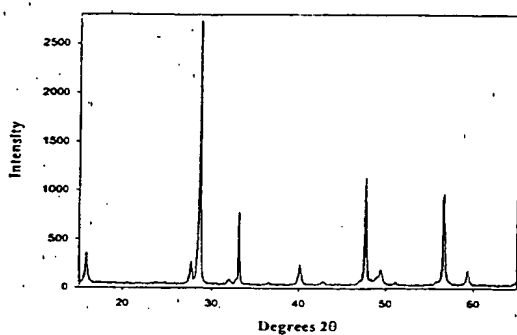


Figure 10(a)

praseodymium oxide

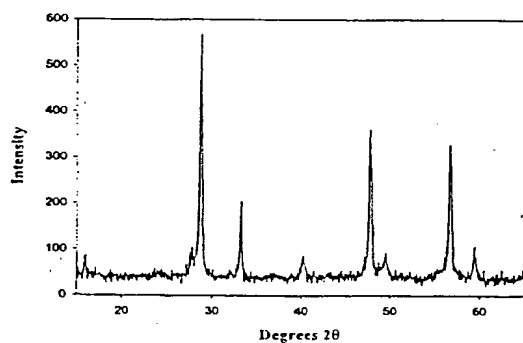


Figure 10(b)

5 wt % Ni on praseodymium oxide

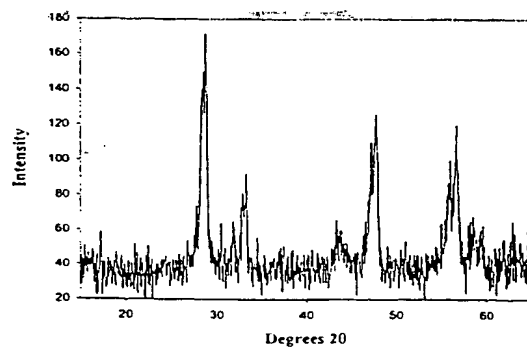


Figure 10(c)

30 % Ni on praseodymium oxide

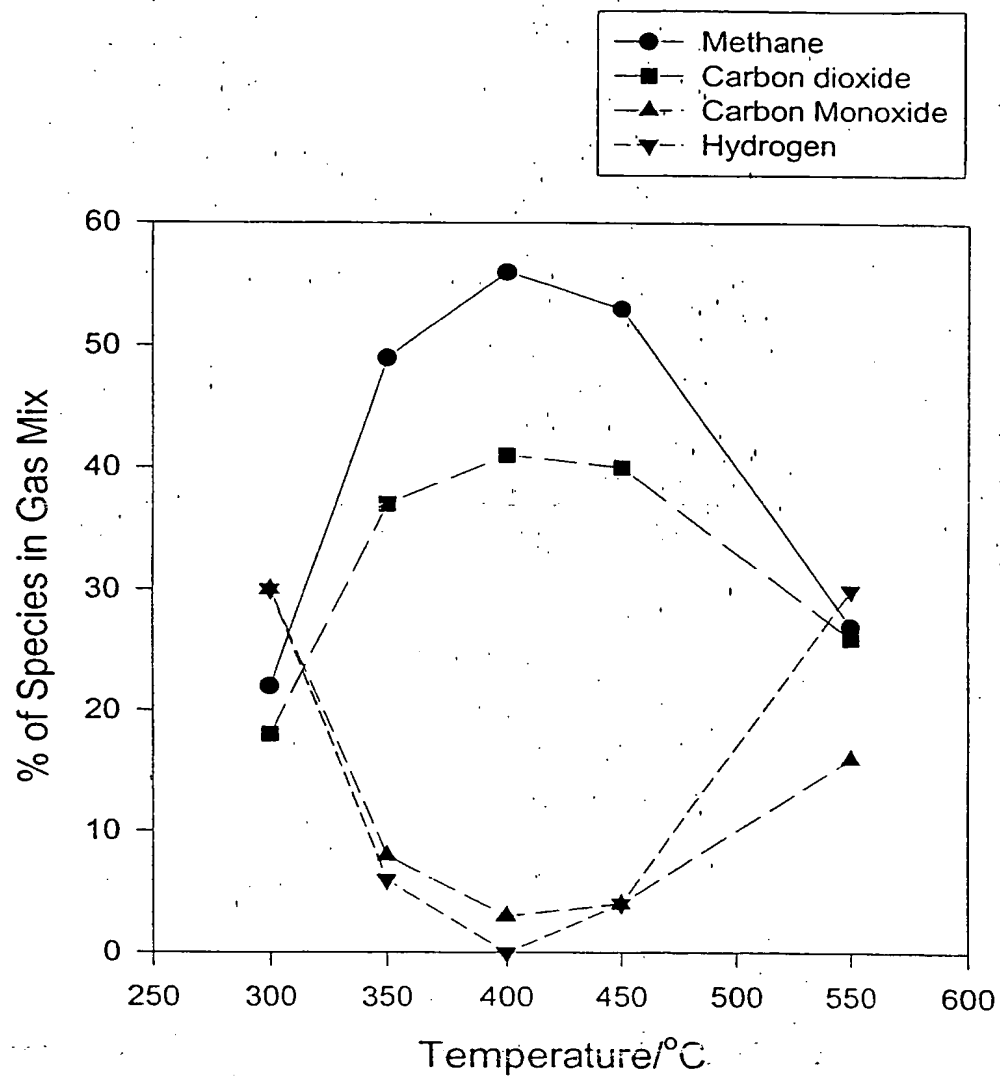
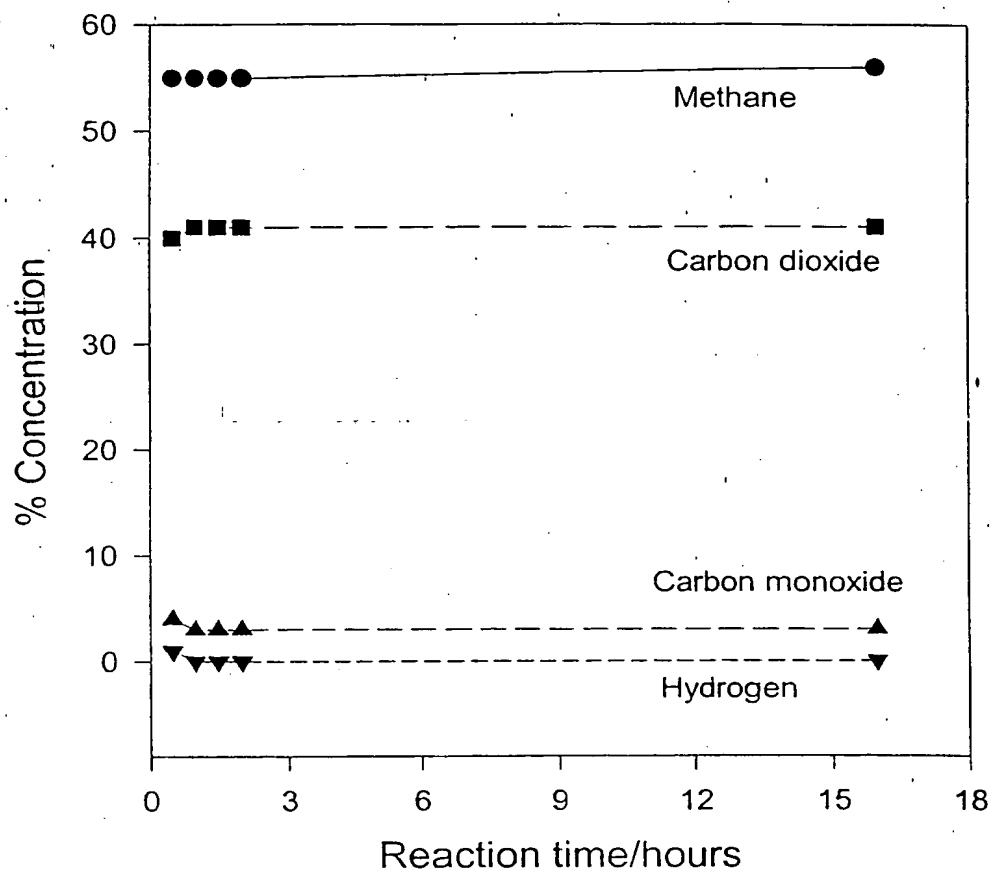
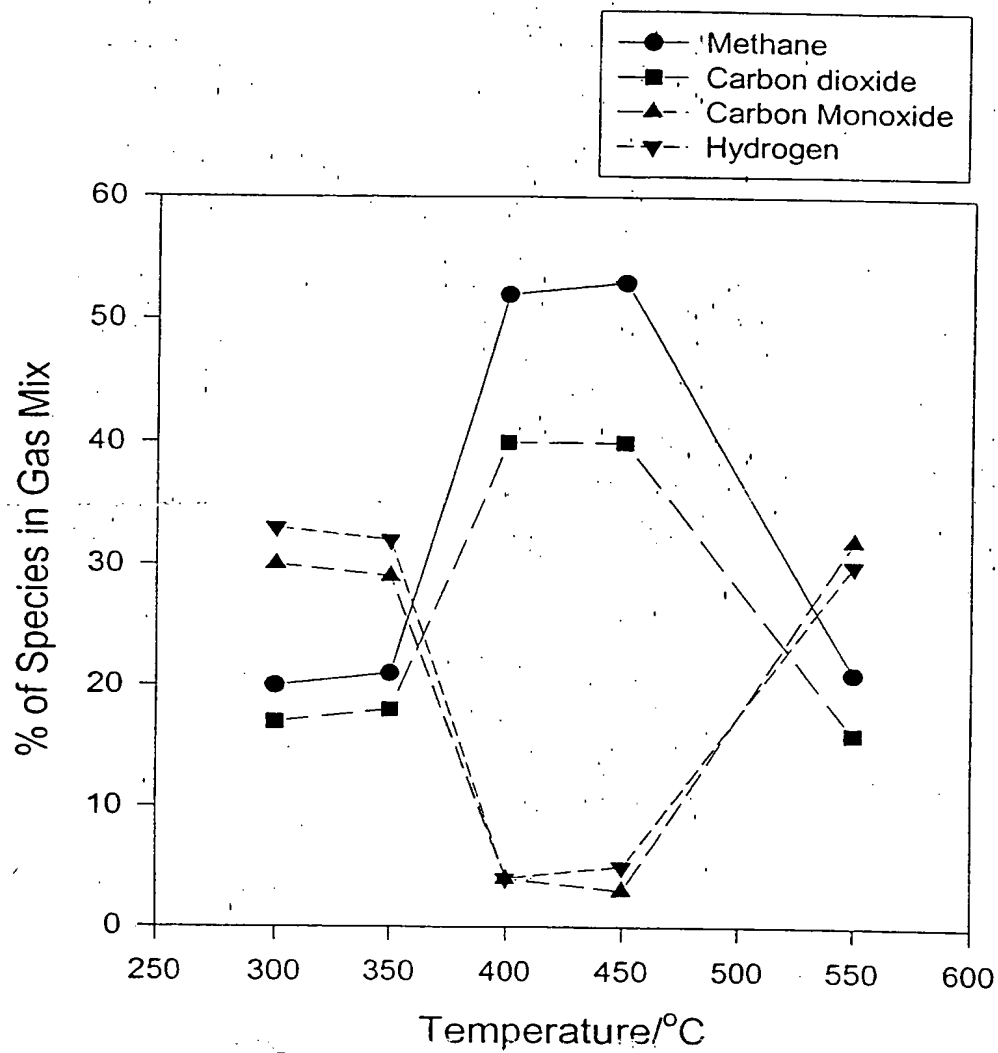
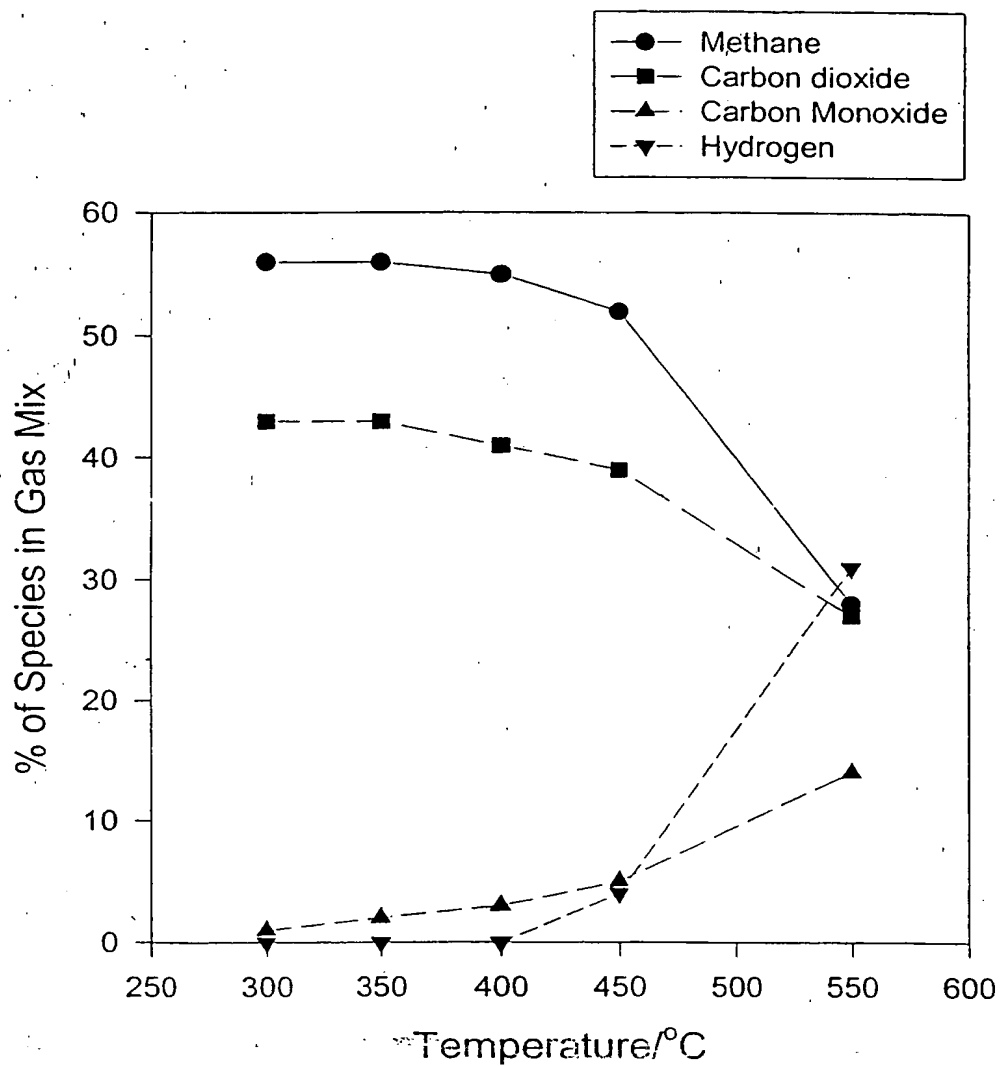


Figure 11

**Figure 12**

**Figure 13**

**Figure 14**

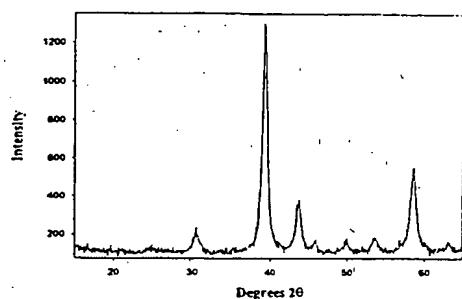


Figure 15(a)

high surface area yttrium oxide

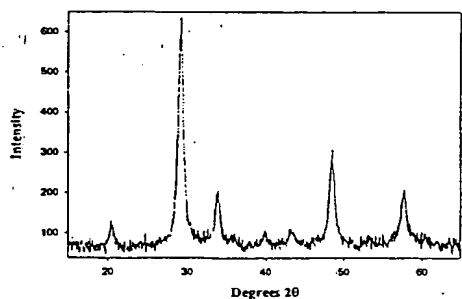


Figure 15(b)

5 wt % Ni on high surface area yttrium oxide

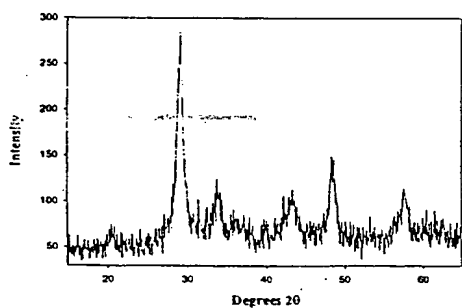
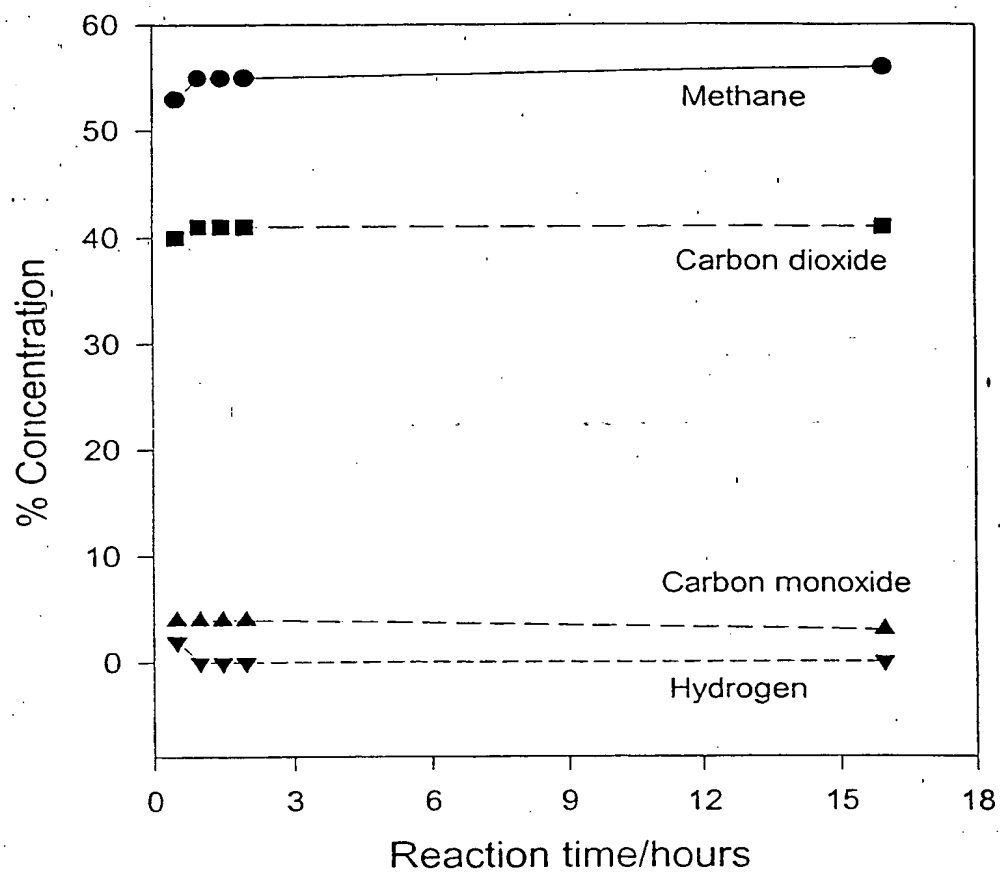


Figure 15(c)

30 % Ni on high surface area yttrium oxide

**Figure 16**



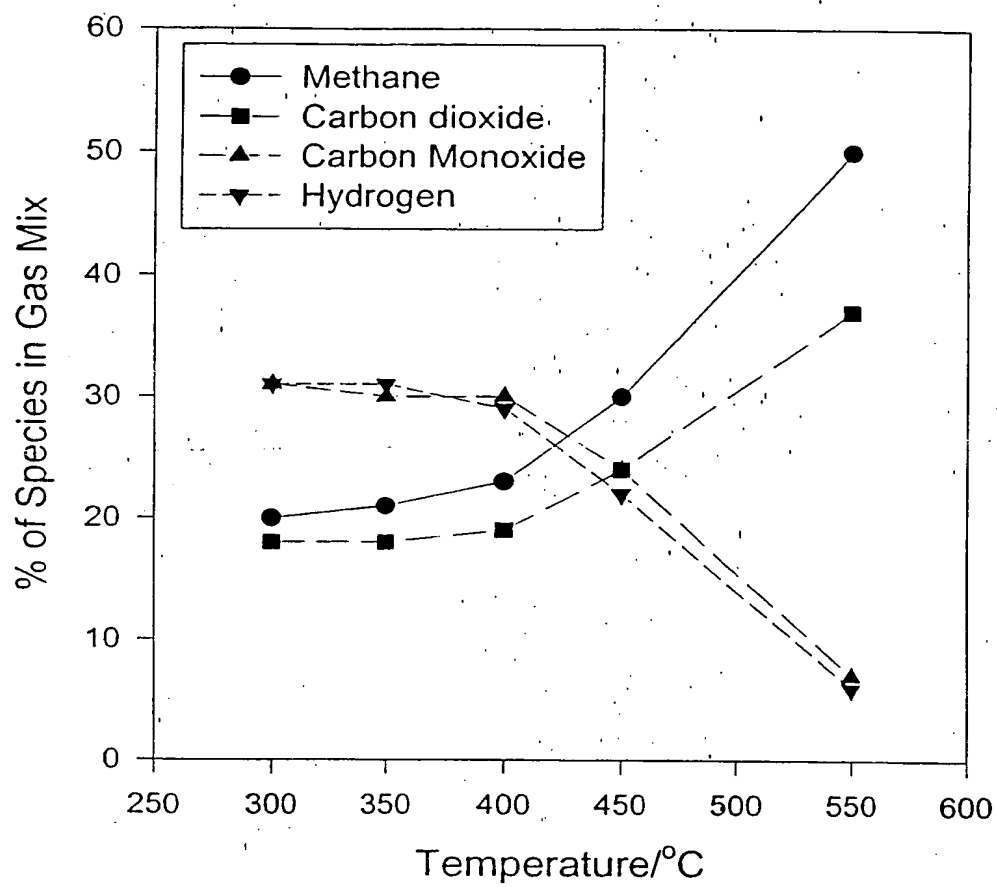
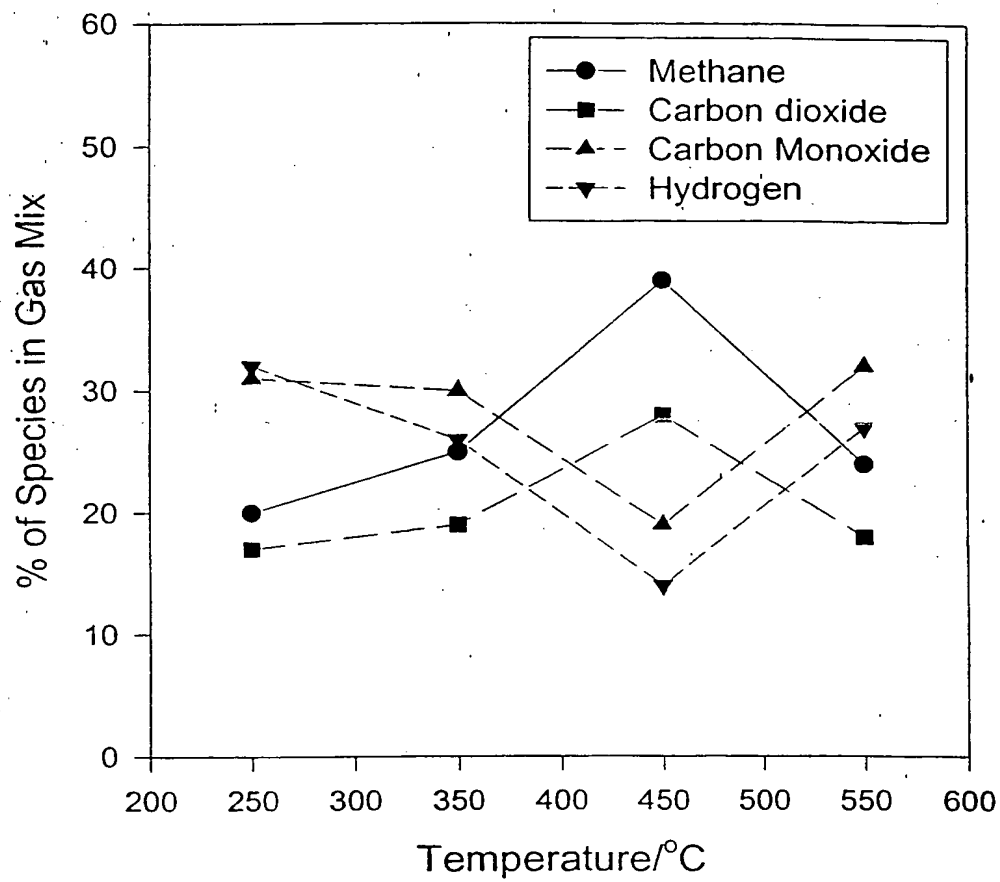
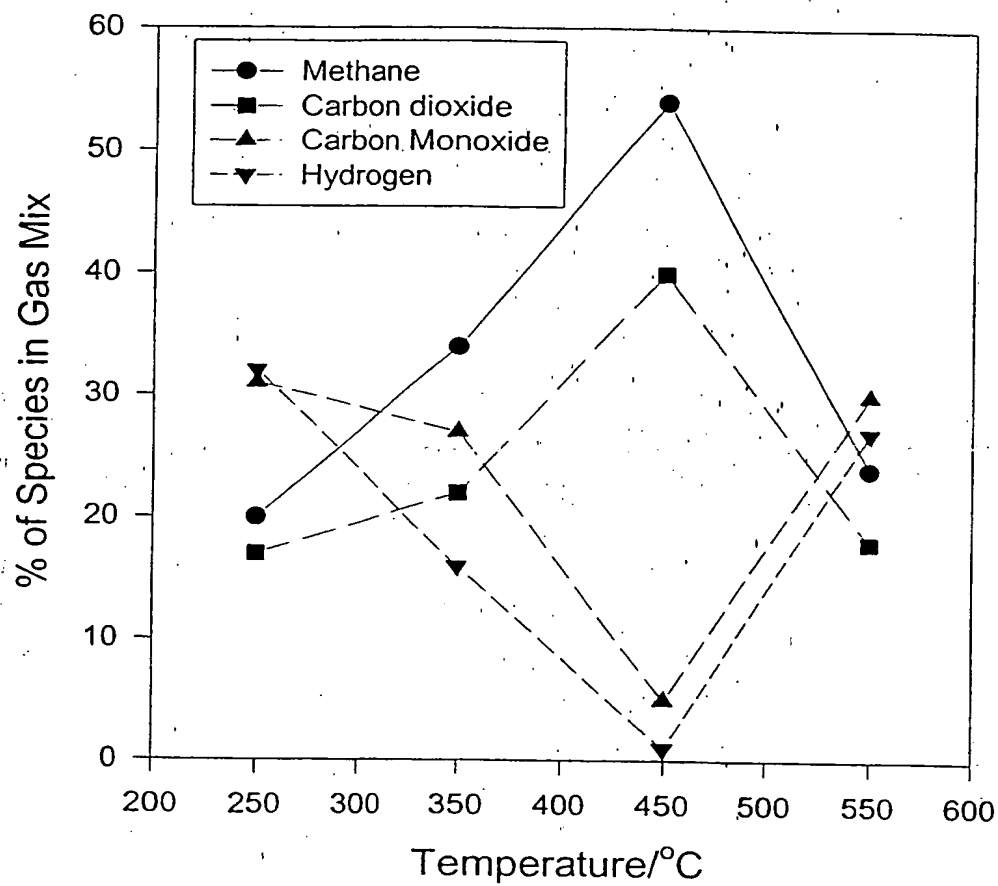
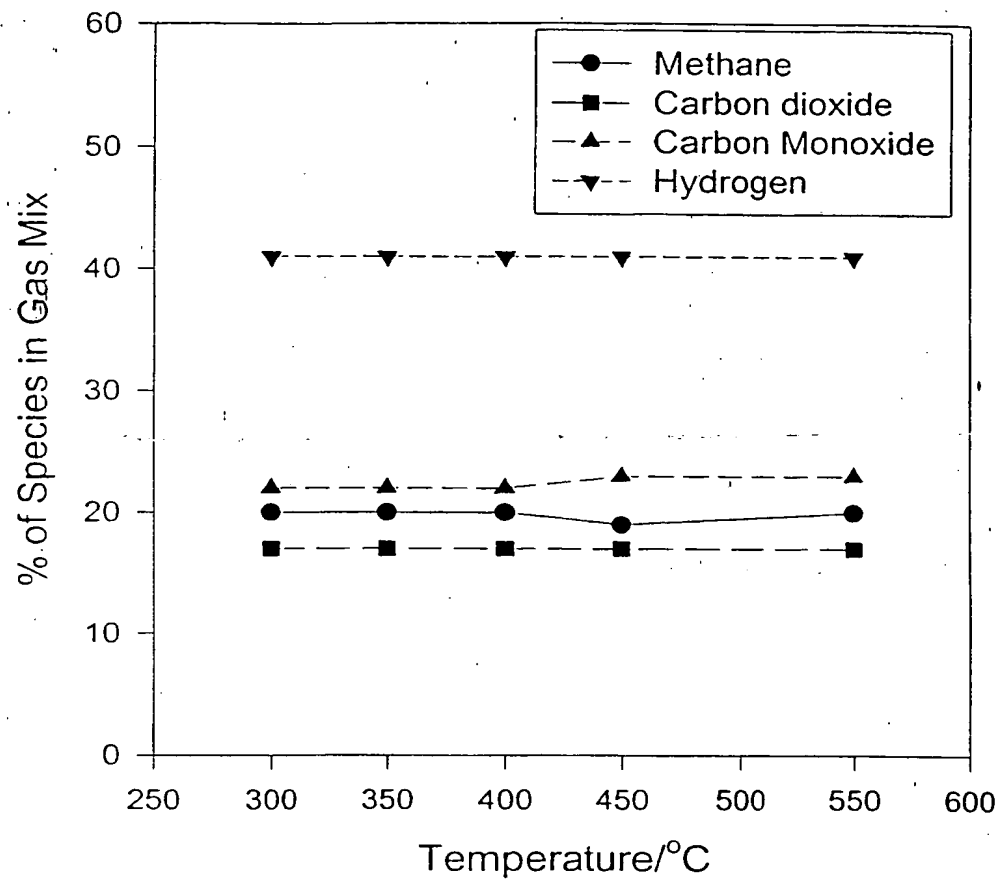


Figure 17

**Figure 18**

**Figure 19**

**Figure 20**

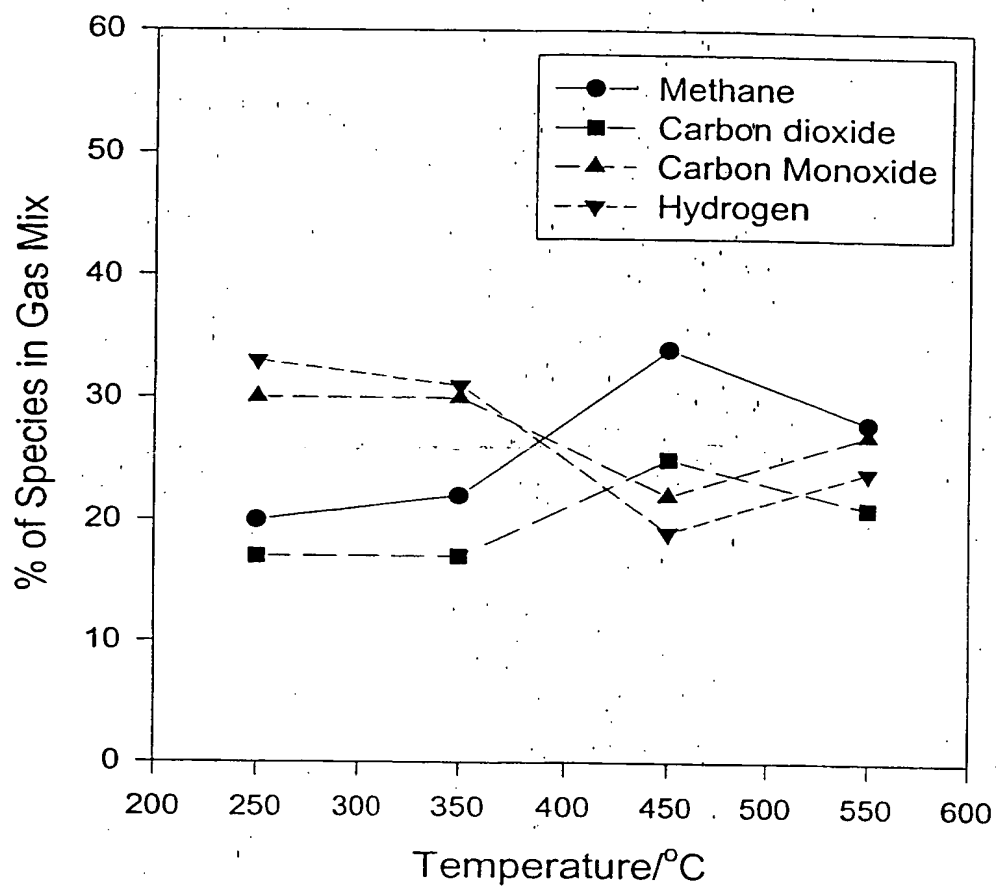
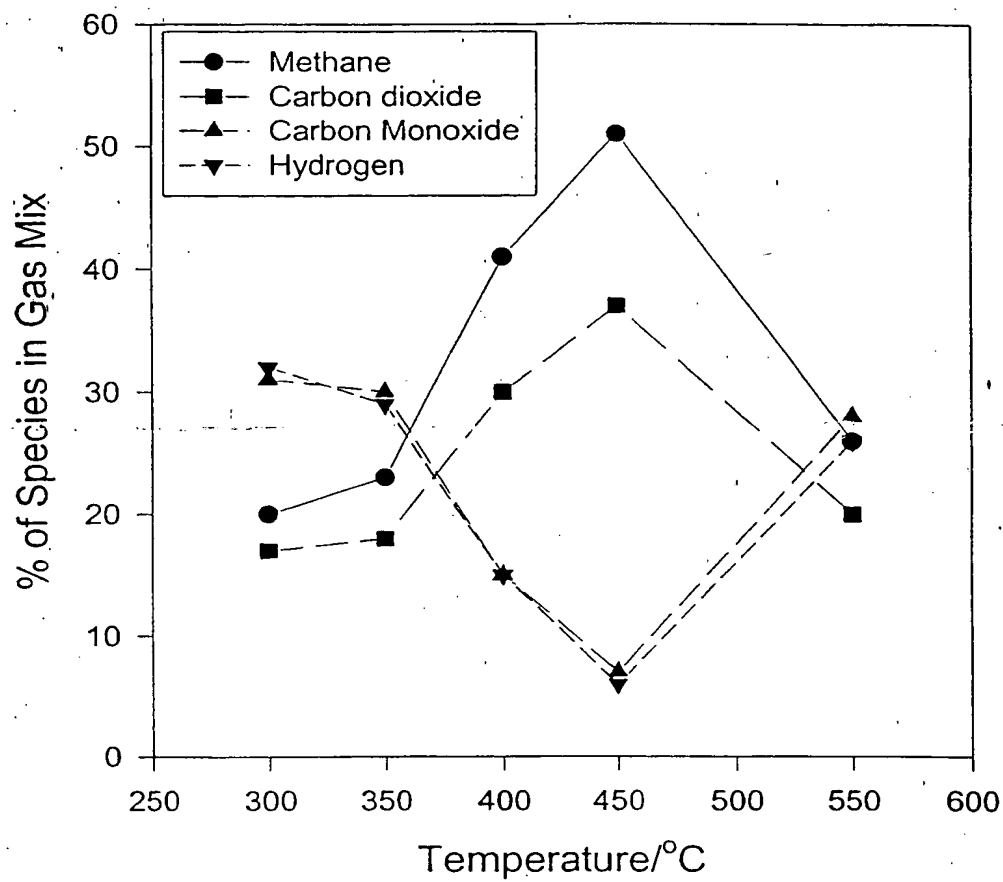
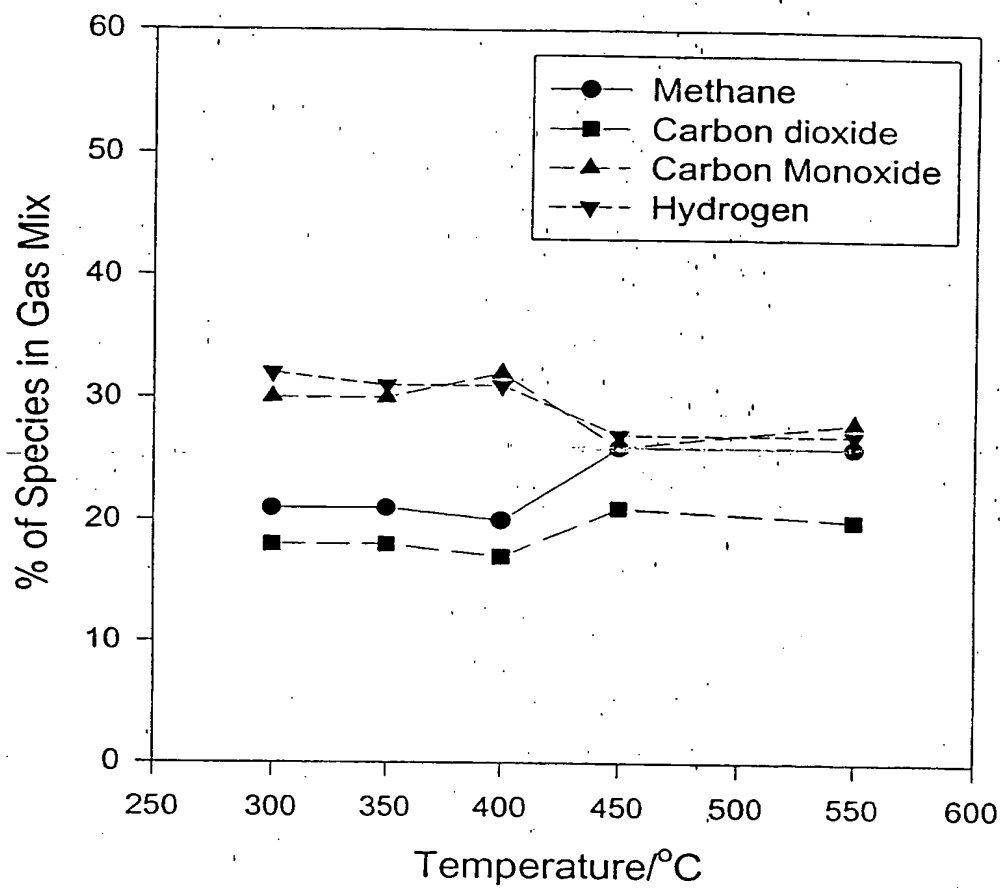
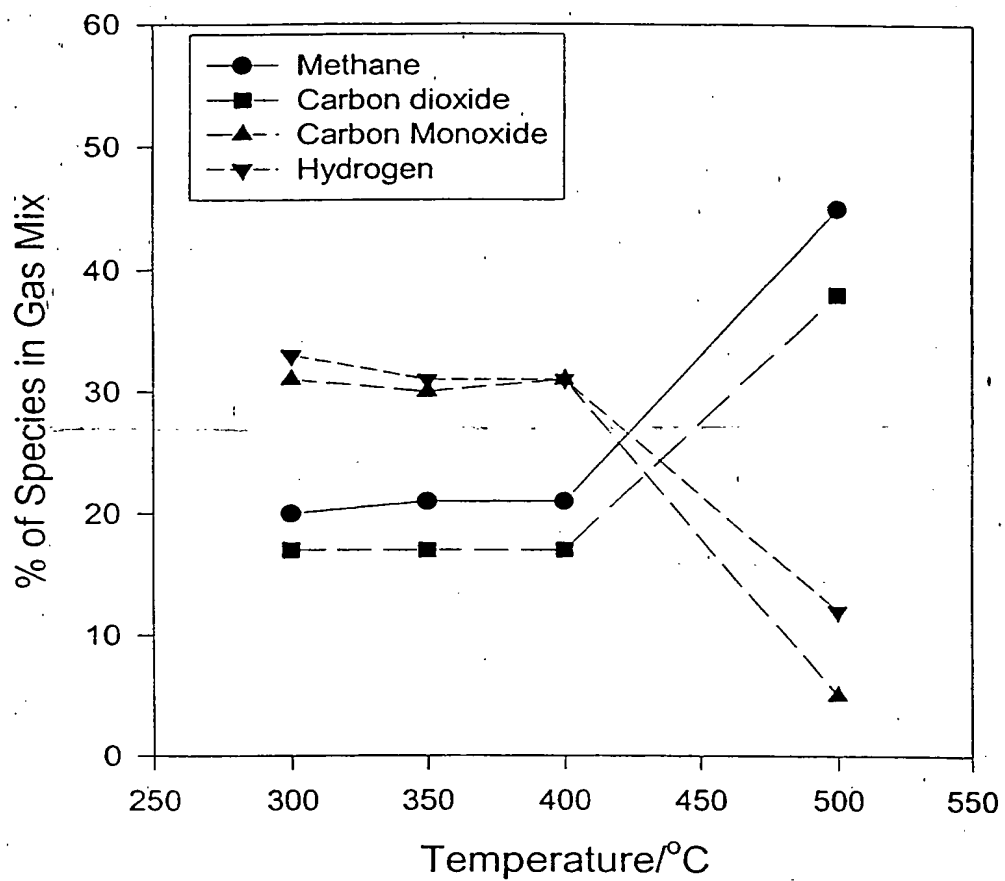


Figure 21

**Figure 22**

**Figure 23**

**Figure 24**



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU 99/00804

**A. CLASSIFICATION OF SUBJECT MATTER**

Int Cl<sup>6</sup>: B01J 23/83

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC as above

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Derwent WPAT

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 98-000458/01, Class E17 J04, CN 1131582-A (UNIV HUANAN SCI & ENG) 25 September 1996	1
X	WO 96/00613 A (KANG) 11 January 1996 See whole document	1,5
X	Derwent Abstract Accession No. 97-345582/32, Class E36 J04 (J01), JP 09141103-A (KYOCERA CORP) 3 June 1997	1,5

☒ Further documents are listed in the continuation of Box C

☐ See patent family annex

<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>		<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  
17 November 1999

Date of mailing of the international search report  
22 NOV 1999

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00804

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP-A1-467363 (TOSOH CORPORATION) 22 January 1992 See examples 7-12	1,5
X	Derwent Abstract Accession No. 87-274317/39, Class J04, JP 62191045-A (AGENCY OF IND SCI TECH) 21 August 1987	1,3,5
X	Derwent Abstract Accession No. 89-030013/04, Class E36 J01, JP 63305938-A (TOYOTA CENT RES & DEV) 13 December 1988	1
X	Derwent Abstract Accession No. 88-107712/16, Class J04, JP 63054938-A (DAINICHISEIKA COLOR CHEM (MATU)) 9 March 1988	1
X	EP-A-468127 (PEKING UNIVERSITY) 29 January 1992 See claims	1

# INTERNATIONAL SEARCH REPORT

## Information on patent family members

International application No.

PCT/AU 99/00804

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	96/00613	CA	2170408	US	5752995		
EP	467363	AU	81105/91	CA	2046951	DE	69129283
		JP	4078445	US	5514355		
EP	468127	AU	71383/91	BR	9101466	CA	2033354
		CN	1058357	DE	69101951	US	5242881
		US	5443807				
END OF ANNEX							